

Report No. CG-D-30-79



A Feasilility Study of the

State-of-the-Art of Personnel Monitors

D. B. Lindsay R. S. Stricoff



NOVEMBER 1978

FINAL REPORT

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Prepared for

U.S. DEPARTMENT OF TRANSPORTATION
United States Coast Guard
Office of Research and Development
Washington, D.C. 20690

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TABLE OF CONTENTS

I. SUMMARY AND CONCLUSIONS II. BACKGROUND II. PROGRAM OBJECTIVE	1 5 6 7 11
	6 7 11
II. PROGRAM OBJECTIVE	7 11
	11
IV. SCOPE OF WORK AND METHOD OF APPROACH	
V. SOURCES OF INFORMATION	
VI. FINDINGS	13
A. TASK I: DEFINE REQUIREMENTS	13
1. General Considerations	13
2. Spill Response Scenarios	14
 Personnel Monitor Design Criteria 	17
 Environmental Conditions of Use 	18
5. Sensitivity Evaluation	20
6. Durability	39
7. Power Requirements	40
8. Hazardous Materials	40
9. Maintenance	40
10. Complexity	41
11. Signals	41
B. TASK II: SURVEY OF PERSONNEL MONITORS	42
1. General Observations	42
 Oxygen Deficiency Monitors 	42
3. Flammable Vapor Monitors	49
4. Toxic Gas and Vapor Detectors	50
C. TASK III: EVALUATIONS AND RECOMMENDATIONS	68
1. General Remarks	68
Oxygen Deficiency	70
3. Flammable (Explosive) Limits	70
4. Toxic Vapors 5. Monitor Combinations Accession For	71
5. Monitor Combinations	74
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NTIC TAB	
DOC TAB Unamnounced Unamnounced	-
Unamnounced Justification	
	-
By	-
Distribution Distribution	109
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pist specific	
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TABLE OF CONTENTS (Continued)

			Page
V11.	GENI	ERAL CONCLUSIONS	80
	A.	CAPABILITIES AND LIMITATIONS OF PRESENTLY- AVAILABLE DEVICES	80
	в.	OPPORTUNITIES FOR IMPROVEMENT OF EXISTING DEVICES	81
		 Piezoelectric Detectors Schottky Barrier or n-p Junction Devices 	81 82
	c.	OUTSTANDING UNSATISFIED REQUIREMENTS	82
	D.	RECOMMENDATIONS FOR FURTHER U.S. COAST GUARD ACTION	86

LIST OF TABLES

Table No.		Page
1	Availability of Personnel Monitoring Devices and/or Technology for CHRIS Substances	21
2	Chemical Categories of CHRIS Substances	36
3	Toxic and/or Flammable Gas Detectors	43
4	Relative Photoionization Sensitivities for Various Gases	63
5	Comparison of the Relative Sensitivities of the Photoionization and Flame Ionization Detectors	65
6	Substances from Table C-2 Having TLV(C) Values	69
7	Integrated Personnel Monitoring Systems Currently Available from Commercial Vendors	76
8	Coatings for Piezoelectric Detectors	83
9	High-Priority Hazardous Vapors for Which No Satisfactory Detector is Currently Available	88
	LIST OF FIGURES	
Figure No.		Page
1	Steps Comprising a Response Action	15
2	SnO ₂ Band Structure	52
3	Resistivity of SnO ₂ :Sb	54
4	Rectifying Barrier Devices	84
. 5	Effect of H_2 Gas on I-V Characteristics of Schottky Barrier Device	85

I. SUMMARY AND CONCLUSIONS

This final report presents the results of a seven-month program of research, study and evaluation of the feasibility of providing an integrated system of personnel monitors, based on currently available technology, that can give prompt warning of a variety of chemically hazardous conditions to which Coast Guard emergency response personnel may be exposed in the course of their work. The desired monitoring devices should be small enough and light enough to be carried by an individual on his person without severely encumbering his activities, and should be able to warn him of the designated hazardous condition spontaneously and without any voluntary effort on his part.

Four types of environmental hazards were identified for which monitoring was desired:

- a) deficiency of respiratory oxygen (i.e., less than 19.5% in air),
- presence in the environment of any combustible vapor above its Lower Flammable/Explosive Limit (LFL or LEL),
- c) presence within a respiratory protective garment of any toxic vapor at a level considered immediately dangerous to life and health (IDLH), and
- d) presence of a potentially dangerous condition with respect to the integrity of protective clothing.

A number of types of personnel monitors were found to be currently available on the commercial market, but most of them are suitable only for non-specific detection of such things as combustible vapors at concentrations approaching the flammable limits, or they are intended for single functions such as warning of oxygen deficiency or warning of the presence of specific toxic gases such as hydrogen suifide or carbon monoxide. A very few of these devices offer combined functions, and those are generally limited to oxygen deficiency and either a flammable limit warning or one or more toxic gases. Only one commercial device was found that would provide all three types of warnings simultaneously, using three sensors. No device was found that would indicate dangerous degradation of protective garments. Thus, an integrated system that would provide all four types of warning is apparently not available from any commercial source at this time.

In order to determine whether the development of an integrated system is technologically feasible, using available sensors, circuitry and packaging systems, we organized our investigation into four separate tasks. In Task I we applied information from our own experience, and that of the Coast Guard, from technical literature, from manufacturers'

literature and from personal interviews to define the requirements of the desired monitoring system. In Task II we conducted a thorough search of recent technical literature, using computer-assisted searching techniques in conjunction with the skills of human researchers, together with a search of manufacturers' advertisements and informational brochures, to determine what devices, components and technologies are available that would be applicable to the task of constructing an integrated personnel monitoring system. In Task III we assembled, reviewed and evaluated the data from Task II in relation to the requirements set forth in Task I, in order to select from all applicable resources the types of components that seemed to offer the best characteristics for the desired purpose. In this connection, we developed a tabulation of pertinent physical and chemical properties of 400 high-priority hazardous materials from the CHRIS list of over 900 chemical substances, and evaluated each of them with respect to its need for detection as a toxic and/or flammable vapor. Each of the resulting group of 188 substances for which a first-priority need was identified was then evaluated with regard to the type of sensor that would detect it in air at the lowest level of concern for short-term exposure. Alternative technologies for detection of these substances were also identified, recognizing that some of these alternatives have not yet been developed to the point at which all the requirements for a personnel monitor can be met in a single commercial product.

In Task IV we considered the feasibility of combining various monitor components into integrated systems in which some saving in space, weight, power and/or cost might be achieved through the use of single components for multiple purposes. For this evaluation we were limited to information provided by manufacturers and technical investigators, rather than having the benefit of direct examination and experimentation with the hardware itself. Thus, the question of compatibility of components could be dealt with only in principle, and conclusions arising from this portion of the work must therefore be regarded as tentative in nature, pending the outcome of more detailed investigation and design studies.

Finally, we have made a number of general observations and conclusions about the capabilities and limitations of present devices, how those capabilities might be enhanced, and what requirements may yet remain unsatisfied. In particular, it appears that two areas are in need of constructive action in order to meet the Coast Guard's ultimate objectives.

First, the area of toxic vapor monitoring shows the greatest gaps in capability. Oxidizable organic vapors are generally detectable in a range extending from the LFL region of a few percent by volume in air ($\sim 10^4$ ppm) down to as little as 10 ppm for some substances, or more generally to about 100 ppm by use of a catalytic oxidation detector or a surface-reactive semiconductor detector. These detectors have very little compound-specificity, however, so that in the presence of a large quantity—say 10^3 ppm—of a relatively non-toxic gas, a smaller quantity—say 50 ppm—of a highly toxic one may go undetected if the alarm level is set to ignore the higher concentration of the less

toxic substances. Setting the alarm at a level that will give adequate warning at 50 ppm will obviously incur an undesirable false-alarm frequency for the more abundant species. Whenever more than one hazardous substance may be present, and the levels of concern for the separate vapors are substantially different, the detector(s) must have the ability to discriminate among them. Very few existing personnel monitoring devices have enough selectivity to be useful in such a situation. Technologically-feasibile solutions are available, but as yet they have not been effectively applied to this problem.

For some highly-toxic substances, notably certain inorganic gases such as bromine and fluorine, no suitable personnel monitor was found to be commercially available. Again, technologically-feasible solutions appear to be available, and some attention should be given to the application.

In comparison to the need for adequate detector capability for specific toxic gases, the problem of system integration appears to be a relatively minor one, involving some design problems of no more than moderate complexity in most instances.

The second area that we found to be in need of attention is that of the development of monitors to warn of incipient damage to protective garments and equipment. We have attempted to provide some guidance and a few suggestions as to how this sort of monitoring might be accomplished, but inasmuch as the requirements for performance of such devices would be rather different from those of the other types of monitors considered here, their development should probably be undertaken in connection with the design and development of the protective garments themselves.

In summary then, we have found that generally satisfactory devices appear to be commercially available for detection of oxygen insufficiency and for the detection of concentrations of combustible vapors approaching the LFL/LEL range. In addition, our research shows that personnel monitoring devices now exist which are capable of detecting most of the substances in the CHRIS list that have vapor pressures high enough to allow them to be present in the atmosphere at concentrations that would be dangerous for short-term exposure. While the CHRIS list may not include all the substances that might be present in the environment as a result of chemical reactions induced by fire, hydrolysis or contact with other substances, the list includes examples of virtually every type of chemically reactive substance, and it seems likely that a set of detectors designed to cover that list will be adequate for the detection of their reations products as well.

Therefore, the answer to the question "Is the development of a multi-functional personnel monitoring system feasible?" is clearly "Yes!" The variety of sensors needs to be extended to cover all the important toxic gases to which strike team personnel may be exposed; selectivity

of toxic vapor monitors needs to be enhanced, and new monitoring concepts for integrity of protective garments need to be explored and developed. Integration of these principles into efficient and effective systems is, in our opinion, a reasonably straightforward and feasible task.

II. BACKGROUND

The Goast Guard has among its responsibilities that of responding to the discharge of hazardous chemicals into or near the waters of the United States. In meeting this responsibility, Coast Guard personnel (including the Atlantic, Pacific, and Gulf Strike Teams as well as local COTP staffs) are expected to encounter situations requiring entry into hazardous environments. In rescuing overcome personnel, assessing damage to tanks and pipelines, implementing emergency repairs to stop the discharge of hazardous materials, and handling discharged material, Coast Guard personnel may be required to operate in an environment containing toxic, corrosive, and/or flammable liquids, solids, and vapors.

In order to properly protect personnel involved in chemical discharge response, the Coast Guard has been concerned with the development of personal protective equipment. This equipment must be capable of preventing skin contact with hazardous liquids, solids, and vapors, as well as ensuring protection against the inhalation of toxic materials. In order to afford the required protection to response personnel, the Coast Guard has selected for immediate use a modified version of the U.S. Army's Protective Outfit, Toxicological Microclimate Controlled (POTMC). The initial model of this suit will be used in conjunction with an air-purifying back pack; however, the Coast Guard has initiated work on the development of a self-contained air supply to be used with the modified POTMC.

In conjunction with the protective suit, the Coast Guard has determined that there is the need to provide an integrated monitoring system that can provide field indication of oxygen deficiency, toxic materials in the breathing air, flammable atmospheres, and loss of suit integrity. Since the list of hazardous materials for which response capability is desired (the CHRIS list) includes more than 900 substances spanning many chemical families, and having a wide range of physical properties, the identification of an integrated monitoring system to protect the health and safety of personnel against all of them is an unusually complex task. The present report summarizes the results of a preliminary study of the feasibility of designing such an integrated personnel monitoring system.

III. PROGRAM OBJECTIVE

The objective of the study has been the development of a comprehensive report on the feasibility of providing a system of personnel monitoring devices for use by Coast Guard personnel whose duties involve emergency response to chemical spills and other hazards of exposure to toxic and/or flammable/explosive/corrosive atmospheres and substances.

The study was divided into five separate tasks as follows:

The objective of Task I was to define the requirements and desirable characteristics of a monitoring system to be used for protection of individual Coast Guard personnel whose work may occasionally expose them to a variety of hazardous substances.

The objective of Task II was to identify and describe any and all existing devices that could be used, either directly or by adaptation, to meet one or more of the needs of the Coast Guard for monitoring of hazardous conditions described in Task I.

The objective of Task III was to evaluate the devices and technologies identified in Task II and to recommend to the Coast Guard consideration of those monitoring devices and monitoring technologies that will best meet the stated needs that were developed in Task I.

The objective of Task IV was to describe possible combinations of monitoring devices that can be repackaged into a single unit which will more effectively meet Coast Guard monitoring requirements then presently available single devices.

The objective of Task V was to present the results of the investigation in a final report.

IV. SCOPE OF WORK AND METHOD OF APPROACH

This investigation was intended to examine the state of the art in personnel monitoring and in closely related technologies, with special emphasis on the detection of toxic, flammable and other chemically-reactive substances present as gases and vapors in the air. A secondary objective was that of examining the feasibility of providing monitoring systems to give timely warning of incipient damage to the integrity of protective garments and equipment. Investigation in both of these areas was limited to acquisition and examination of published information, both technical and commercial, and to correspondence and conversations with knowledgeable persons. Evaluation of the collected data and development of recommendations were based on the professional experience and judgment of our own staff and consultants. No new experimental or test data were intended to be developed and all information on the performance and characteristics of devices that were considered was provided from other sources.

Criteria for performance of the desired personnel monitors were developed in collaboration with the Coast Guard, and with information based on our own experience with requirements for similar devices in various domestic, military and industrial situations as well with those of the Coast Guard. Qualitative identification of specific hazardous substances was not a requirement of the desired monitors, since the Coast Guard wished to proceed on the assumption that the identity of any hazardous substance present in any particular instance would be known by other means. The monitoring system was therefore required only to have a known (and sufficient) sensitivity to any named substances(s) so that it can provide a warning if and when a dangerous concentration of that substance (or combination of substances) occurs in the individual's immediate environment.

While the ability to continuously measure oxygen concentrations in the region of 19-20% is a reasonably specific requirement, and that of detecting flammable/explosive limits is moderately specific in that it applies to an empirical analog of flammability for any oxidizable hydrocarbon, the detection of toxic levels of all of the 900 hazardous chemicals in the CHRIS list was recognized to be a much more complex task. OSHA Standard Levels for these substances in air range over at least three orders of magnitude, and, from a toxicological standpoint, substantial differences exist between substances that may be detectable at virtually identical limits by any applicable sensing system. For economy, simplicity and practicality one would prefer to have a minimal number of separate detectors and/or sensors to cover the range of materials and concentrations of concern.

When more than one substance is present and detectable, however, the need for separate selective detectors may be inescapable. Problems such as this were recognized at the outset, and it was acknowledged that additional field experience would probably be required before a truly satisfactory set of requirements can be developed to meet the needs of the strike teams.

Our approach to this problem was essentially that which we outlined in our proposal of June 27, 1977. In general, we used a combination of existing information, published literature and personal interviews to define the requirements of the desired monitoring system capabilities in Task I. Task II also involved some personal interviews, in this case, with developers and manufacturers of available monitoring devices. Task II included a thorough search of our technical and manufacturers' literature and made use of our formal literature-search facilities. Our approach to Task III involved intensive study and discussion among the several members of the study team, representing areas of industrial experience and professional expertise that were especially relevant to the subject problem. Evaluations and recommendations were carefully reviewed by the program director with assistance from our consultant, Mr. Adrian Linch, a noted authority on the subject of personnel monitoring and protective equipment, and the U.S. Coast Guard Project Officer, Lt. D.D. Rome.

Task IV involved creative study by members of the project team experienced in the development of physical and chemical sensing systems, instruments and monitors and sampling devices, and in the interpretation of the various elements required into working devices that meet the specific requirements of a given situation.

In defining performance requirements for a Coast Guard response personnel monitoring system in Task I, an attempt was made to generically describe the elements of a response action. That is, rather than anecdotally relating the descriptive parameters of specific incidents (real or hypothetical), the steps comprising a response action were listed, and the important elements of each (and the variations possible) were described.

Based upon the generic description of response actions, specific performance criteria were prepared to provide a benchmark in judging whether a postulated Coast Guard personnel monitoring system will operate reliably and effectively during actual use conditions. Each of these criteria has been listed in Section VIA of this report and is accompanied by a brief explanation of its necessity.

From the standpoint of a designer of a universal hazard-warning system, it was clear that some compromises would have to be made between the desired objectives of providing a reliable instant warning for any of the potential hazardous conditions, and of incorporating that array of capabilities in a single compact unit that could be worn on the person without encumbrance or discomfort. In the interest of determining exactly what the primary needs of pollution response personnel are in

this respect, and of establishing priorities for attributes that are essential, highly desirable, only moderately desirable, or even unnecessary, we collected information from personnel experienced in chemical spill response work, and supplemented their experience with a review of available incident reports. Our personal contacts included representatives of the Coast Guard (Strike Teams, headquarters' staff, and COTP personnel), industrial and trade association response groups, and other interested government agencies. We reviewed the capabilities desired in a monitoring system for field use, and the important limitations such as maintenance, power supply, size, and weight. We also reviewed available chemical discharge incident reports, paying particular attention to the information needs of responding personnel and the environmental conditions under which response was undertaken.

The development of performance criteria for a monitor system to warn the wearer of a potentially dangerous condition with respect to the integrity of his protective clothing and equipment presents a set of problems that were seen at the outset to be rather different from those involved in warning of atmospheric pollution by toxic or flammable gases. Most protective equipment is virtually impervious to the effect of such low concentrations of materials, and is much more resistant to the effect of most chemical substances than is the human body. Even the best protective equipment is not resistant to the attack of some of the most corrosive chemical and powerful solvents, however, and since protective clothing lacks the inherent warning systems that the human body's nervous system provides, some substitute system is needed to give warning of such a destructive attack.

Since virtually all of the substances that would present any substantial threat to the integrity of protective clothing are likely to be in liquid form (rare exceptions would be metallic sodium or potassium, and a few other reactive solids, and some highly reactive gases such as fluorine) and to be dangerous only on contact with the protective equipment itself, detection of the dangerous situation would probably have to be limited to actual contact rather than to proximity of the hazardous substance. This would mean that some special sensing system (analogous to the sense of touch, but communicating immediately to a visible or audible alarm) would have to be built into the outer surface of the protective equipment. Warning in this case might have to be exceedingly prompt in order to avoid a potentially rapid and catastrophic failure. Nevertheless, since the only alternative appears to be one of remote sensing or of test-probing a suspicious substance, neither of which is amenable to continuous automatic sensing, the contact mode appears to be the most practical approach. Inasmuch as this conclusion was only a tentative one and rests on a number of assumptions that need to be tested in practice, we limited our approach here to exploring some options for such a system.

Our investigation in Task II involved a thorough search of published technical literature, covering the sources identified in Section V below, and using the methods of computerized searches as an adjunct to the work of technically trained literature researchers. Abstracts of relevant articles were furnished to the Task Manager for consideration by individual team members, who then decided whether the full text of any original publications needed to be studied.

Team members made contact in writing and/or by telephone with manufacturers of potentially useful devices, and obtained whatever commercial literature that was available and pertinent. Conversations with manufacturers were important in determining how well individual products would satisfy any of the requirements defined in Task I, and how readily one might expect to adapt any of these devices to a combined monitor system that would serve several purposes at once.

Some of the data that were to be obtained for presently-manufactured monitors were in respect to the following attributes: (1) the efficiency of the detector elements for both individual chemical and class detection; (2) the type of warning signal for personnel involved; (3) response times; (4) service life of detector elements; (5) power supply life and renewal capability; (6) effect of the operational environment as well as the weight and dimensions of present units; and (7) physical dimensions and weight of the unit.

Our approach to Task III was to review the results of Task II and to assess the merits and limitations of the various devices, systems and potentially applicable technological alternatives in relation to the data from Task I. Members of the professional staff examined the data, discussed, questioned and re-examined the evidence, and ranked the various candidates in terms of their apparent suitability for the Coast Guard's pruposes. Because so much of the information obtained had to be taken on faith, there being no opportunity to test its accuracy in the course of this project, estimates of suitability were limited to a very few categories: a) presently-available devices with good evidence of demonstrated effectiveness, b) commercially-available devices with limited demonstrability of effectiveness, but showing good promise of applicability, and c) devices and technologies with theoretically arguable applicability, but requiring more extensive development.

Task IV was in effect an extension of the same process used for our approach to Task III. In attempting to conceive, describe and evaluate possible combinations of useful monitoring devices, we applied the experience and judgment of engineers and scientists on our staff in an essentially speculative exercise in which the advantages, limitations, trade-offs and possible problems of integrating different types of monitors were identified and assessed.

V. SOURCES OF INFORMATION

Information and data were developed and organized in two categories:
(a) commercially available products, and (b) applicable technology.
Information about commercial products has been obtained from directories of products and suppliers, as well as from recent trade publications and from data bases such as the reports of Predicasts, Inc.

In addition to personal interviews with developers and manufacturers of devices and with people experienced in marine emergency pollution response work, our sources of information included a formal search of the technical literature for the past thirteen-year period to discover pertinent references to the development of sensors and monitors.

Information about applicable technology in personnel monitoring was obtained by computer searching of the following data bases.

Data Base

Time Frame

1. Chemical Abstracts (CA CONDENSATES) 1970 to December 1977

This index includes more than 1,000,000 references to journal articles, patents and conference proceedings from the world-wide literature for chemistry and chemical engineering from the Chemical Abstracts Service.

2. Engineering Index (COMPENDEX)

January 1970 to December 1977

This data base corresponds to the Engineering Index and covers civil, geological, mining, mechanical and industrial engineering.

3. ENVIRONLINE

January 1971 to December 1977

4. APTIC (Air Pollution Technical Information Center)

1966 to 1977

5. NTIS (National Technical Information 1964 to 1977 Services)

This complete Governments Reports Index/Announcements file from the National Technical Information Service contains over 482,000 abstracts of government-sponsored research from over 240 agencies.

In order to insure a complete literature search, the computerized searches mentioned above were extended on some instances by the use of manual indexing and abstracing sources. These manually searched sources included the following:

Literature Sources

Time Frame

Chemical Abstracts	1964 through 1971
U.S. Government Research Reports	1950 through 1963
Science Citation Index	1965 through 1973
NASA/STAR	1965 through present
Engineering Index	1965 through 1969

In the case of foreign language materials, English-language abstracts were obtained. Special sources were identified and contacted.

 Λ complete bibliography of applicable technical literature and a list of sources of commercial product information are appended to the report as Appendix Λ and Appendix B.

VI. FINDINGS

A. TASK I: DEFINE REQUIREMENTS

General Considerations

The data that we collected in Task 1 were used to construct several scenarios for employment of a monitoring system by persons responding to an emergency involving accidental chemical discharge or spill. These scenarios were designed to point out the extremes of potential use conditions, and to justify and clarify performance requirements.

Based upon the scenarios we developed, we prepared a detailed set of performance requirements for a Coast Guard chemical response monitoring system. While the performance requirements were designed to be sufficiently explicit to permit the evaluation of specific hardware concepts, the emphasis was on performance, rather than specification, standards; thus, no inadvertent bias for or against any monitoring concept or specific piece of hardware could enter into the requirements.

Due to the unique conditions under which Coast Guard response personnel must operate, it is important that any candidate monitoring system be capable of functioning under conditions that, in some ways, may differ greatly from those typical of an industrial environment. Our recent involvement in the development of the Coast Guard's Chemical Hazards Response Information System (CHRIS) gave us important insights into the special problems presented by chamical pollution problems associated with marine activities.

When Coast Guard response personnel are notified that a chemical discharge has occurred, there is certain information which will be immediately available. It is assumed that the identity of the chemical(s) will be known and that the flammability, toxicity, and reactivity of these chemicals can be determined from the Coast Guard's Chemical Hazards Response Information System. Response personnel may have no way of knowing the concentration of chemical vapors and/or solutions present at the discharge site, however, and will not know the oxygen concentration in the area. These personnel will also need to know the adequacy of their protective clothing when challenged by the discharged chemical(s) as well as the "breathability" of the atmosphere and its flammability.

If a monitoring system could be devised to meet the Coast Guard's needs, consisting of only a single unit, many errors in the preselection of appropriate equipment during the staging of a quick response could be avoided. Obviously, such a monitoring system should also be capable of withstanding rough transport and handling as gear is moved to the spill scene, and should be self-powered for use over periods as long as an individual would expect to be on continuous duty in the hazard area. Size and weight criteria should be determined for any unit to

be worn in combination with any sort of work clothing or protective clothing, so that any suggested monitoring system would conform to the practical requirements of minimal encumbrance to the wearer.

There is little doubt that, for "real-time" personal warning systems that will be used by emergency response personnel, an active alarm system is preferable, which, when set for a given trigger-level, spontaneously provides a virtually inescapable visual and/or audible alarm to the wearer. The monitoring system should be capable of operating in a salt-spray environment over wide temperature extremes and at high humidity. It should be capable of withstanding shock, vibration, and immersion during use. The monitoring system may be exposed to massive transient levels of contaminant, and should be capable of recovering sensitivity quickly after such instances. The monitoring system should also be safe for use in flammable atmospheres and, since the system may be used in the field for weeks at a time, any calibration or maintenance that may be necessary at frequent intervals should be easily accomplished under field conditions.

Spill Response Scenarios

As Figure 1 depicts, the response of a Coast Guard Strike Team to a hazardous material discharge can be described as following a number of steps. In order to help to define the conditions under which a personnel monitor might be handled and used, each step in the spill-response sequence has been examined to identify the range of pertinent conditions. The significant parameters of each steps of the response sequence are described below.

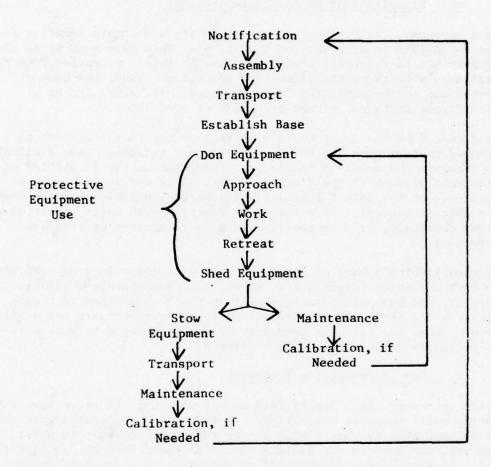
a. Assembly of Equipment

Upon notification of a hazardous material discharge, the Strike Team will assemble with appropriate equipment for assisting in response activities. Such assembly must be rapid, and the need to make choices among alternative items of equipment could be a confusing one. Further, the responding Strike Team must expect to find conditions at the discharge site different from those conditions described in the initial incident report, whether because mistaken information was transmitted during initial confusion or because a change in situation has occurred (e.g., climatic change, chemical reaction, ignition of combustible materials, etc.).

b. Transport

The modes of transportation utilized by Strike Teams and workers to reach the scene of a discharge are many and varied. Virtually every mode of sea, land, and air transportation may be employed, depending upon the availability of transportation and the accessibility of, and distance to, the spill response scene. Thus, Strike Team response

Figure 1
Steps Comprising a Response Action



equipment is designed with an emphasis on "transportability." Extensive use is made of mobile vans, palletizing of equipment, and suitcase packaging of small equipment. In general, it would be desirable for all of the necessary personnel monitoring equipment for one Strike Team to be transportable in a container about the size of an ordinary footlocker.

c. Establishment of Base Of Operations

Once on-scene, the Strike Team must identify a suitable location for the establishment of a base of operations. This base must be as close as possible to the spill scene, but must be safely protected from the hazardous effects of the discharged materials. Thus, the base of operations may be separated from the actual discharge site by a significant distance, either over land or over water.

As dictated by the Coast Guard's objectives for this study, it is assumed that once on the scene, the response personnel have available an accurate and complete source of information on the identifies of chemicals present in the discharge area. This implies not only a knowledge of the material actually discharged, but also implies that any changes occurring as a result of reaction with water, reaction with other chemicals, or decomposition will be recognized by response personnel.

In establishing a base of operations, it will not always be possible to have utilities (electricity, water, gas) immediately available. Further, the base of operations will at times be located in remote areas, where tools and replacement parts or equipment are not available. Thus, the response team must be fully equipped to work self-sufficiently during its response efforts.

d. Use of Protective Equipment

Where necessary, each Strike Team member will use his protective suit during spill response activities. It is anticipated that a work shift of no more than two hours will be the rule when the suit is worn; however, the need to don equipment at a distance from the spill site will, in some cases, necessitate an actual shift of significantly less than two full hours.

The response team protective suit presently planned for issuance to Strike Teams consists of a full protective suit with a back pack providing filtered air for breathing and body cooling. The suit, which includes gloves, boots, and helmet, is fully water- and gas-tight.

Conditions under which the protective suit is used will be widely varied. Ambient temperatures will range from approximately -40°C through 50°C (-40°F through 122°F); however, temperatures within the protective suit will fluctuate within a narrower range. Relative

humidity in the ambient environment will range from 0 to 100%, with humidity within the protective suit remaining fairly high. Winds may be excessive, reaching levels as high as hurricane force under extreme adverse response conditions. Work continues in spite of precipitation (including sleet, snow, freezing rain, etc.). Finally, many spill responses are staged in the corrosive marine environment.

Since speed in mounting a response will often be critical, protective equipment must be ready for use at the spill scene without a large amount of assembly, calibration, or testing. However, because spill response personnel often work under conditions which necessitate concentration on specific tasks, protective equipment must be as fail-safe as possible and should provide an adequate indication of inoperable conditions (e.g., no power).

There are four types of information which will be useful to spill response personnel wearing protective equipment. First, the response team member will need to know of the presence of toxic materials within his suit environment. Second, the wearer will need to be warned of an oxygen deficiency within the suit. Third, it is important to know whether the atmosphere outside of the protective suit is flammable. Finally, it is important to know when physical contact with a chemical is causing a breech in the suit's protection (i.e., penetration). Two of these parameters describe the atmosphere within the protective suit (hazardous material presence and oxygen deficiency), one parameter describes conditions in the ambient environment (flammability), and the final parameter describes the physical integrity of the protective suit itself. Since the response team member's reaction to each of the fourdescribed conditions will vary, it is important to discriminate among these conditions in providing a warning signal. The triggering of the signal should not depend upon an active inquiry from the wearer since he will often be preoccupied by activities requiring the constant use of both hands.

At the conclusion of a two-hour work shift, the protective equipment user will return to his base of operations and will shed his protective clothing. During long-duration response efforts, it will be necessary for protective equipment to be placed in service again within two hours; therefore, any maintenance, calibration, or replenishing of supplies that is necessary must be performed readily under field conditions.

At the conclusion of the response effort, it will be necessary to store equipment and transport it back to the Strike Team headquarters. Since the amount of time available prior to the next response effort might be quite short, stored equipment should be immediately ready for re-use.

Personnel Monitor Design Criteria

Based upon the type of use conditions described above, a set of performance requirements for spill response personnel monitors has been developed. The objective of these performance requirements is to

ensure that a personnel monitor system can be effective and reliable under the challenging conditions in which Coast Guard response teams operate. Within this section, each performance requirement is stated and then followed by an explanation of supporting rationale.

a. Weight

The personnel monitoring system should weigh a maximum of ten pounds, and preferably no more than seven pounds.

Discussions with the Coast Guard regarding the overall weight of their protective equipment and the weight "budget" considered reasonable lead to the conclusion that as much as ten pounds may be acceptable. However, it is considered desirable to minimize the amount of weight that response personnel must carry.

b. Dimensions

The bulk of the personnel monitoring unit should be designed to fit within, or be mounted upon, the back pack unit of the protective suit. Thus, dimensions not exceeding 14" x 8" x 10" are necessary, and smaller dimensions would be highly desirable. (Note, however, that some sensors, such as those designed to detect incipient failure of the protective suit, as well as the present oxygen-sufficiency monitor, must be located in the suit itself.) The choice of a location within or atop the back back unit is desirable in order to help maintain balanced weight distribution throughout the protective suit, and in order to minimize the number and length of leads that are necessary to connect the monitoring unit with the flammability, toxicity, and oxygen probes. This design dictates a width and depth of 14 inches by 8 inches. Avoiding an excessively high profile leads to the recommendation of a maximum 10-inch height. It should be recognized that design of all or part of the monitoring system for mounting elsewhere on the protective suit might be beneficial for a number of reasons, including the increased flexibility of physical dimensions.

4. Environmental Conditions of Use

a. Flammability Sensor

Depending upon the effectiveness of the air-purifying device to be used, the flammability sensor may be mounted either inside or outside of the protective suit; thus, if it must be outside it should be capable of operating under conditions of extreme temperature variation (-40°C through 50°C), relative numidity (0 through 100%), high winds, precipitation and splashing, and corrosion by salt spray.

The environmental conditions listed above are those under which Coast Guard response personnel might reasonably be expected to work.

It should be noted that the present XM 41 air filter is not an effective barrier against most organic vapors when they are present at concentrations approaching the flammable/explosive limits. Thus, the air inside the suit is likely to have virtually the same concentration of flammable vapors as in the air outside it. Therefore, until and unless a relter is used that effectively removes combustible organic vapors from the air, or unless a self-contained air supply is used, the LFL/LEL detector need not be external to the suit.

Also, unless more than one type of hazardous vapor is in the air, such that selective detectors are needed for each substance at its particular threshold concentration of concern, a single detector, set to alarm at the lowest level of concern, will usually be sufficient. With few exceptions that level will be the one associated with human toxicity rather than the LFL/LEL.

In circumstances where a self-contained breathing apparatus is to be used, detection of flammable vapors will need to be done by a sensor placed in contact with the outside air. Explosive-limits detectors, whether catalytic or semi-conductor types, can be operated effectively within protective cages or housings incorporating five stainless steel screens or frits which permit passage of gases and vapors, while effectively blocking droplets of liquid or solid particles. These shields are provided as standard equipment on most devices of this kind. To provide additional protection against splashing by salt-water spray or contaminants by chemical fogs, an additional protective housing could easily be provided for the detector with baffled louvers to prevent flooding of the unit, but permitting free flow of air to it. The entire detector unit, which is small and light, should be mounted on the face-piece of the self-contained breathing appratus in order to afford it maximum protection against hazards. (Mounting in a location near the eyes has the advantage that the wearer instinctively protects his eyes from splashing liquids, projectiles, etc., and thus is likely to offer the same protection to the detector.)

b. Toxic Material Sensor

The toxic material sensor should be designed to operate under relative humidity levels ranging between 0 and 100%, and temperatures ranging between -40°C and 50°C. This sensor should also be resistant to salt spray corrosion.

Although the toxic materials sensor will be located within the protective equipment, it may be called upon to operate under temperature extremes, particularly during the initial stages of a work shift. While this sensor will be shielded from winds during its use, it may be exposed to the corrosive marine environment when the suit is not actually being worn.

c. Oxygen Deficiency Sensor

The oxygen deficiency sensor should operate under the same environmental conditions as the toxicity sensor.

This sensor, which is also located within the protective suit, will be exposed to environmental conditions identical to those challenging the toxicity sensor.

d. Suit Integrity Sensor

The suit integrity sensor system should operate under conditions identical to those described for the flammability sensor.

Like the flammability sensor, the suit integrity sensor can be exposed to ambient conditions. By definition, it must be designed and located so that it will detect any actual or incipient breach of the suit's integrity anywhere on its surface.

Sensitivity Evaluation

a. Flammability Sensor

The flammability sensor should be capable of detecting flammable concentrations of vapors of any substance in the CHRIS list.

Of the more than 900 substances now listed in CHRIS, only about a third are combustible in air and are sufficiently volatile to exist in air * at 40°C at concentrations approaching the Lower Flammable Limit (LFL). The names of these substances are listed in Appendix D. Table 1 lists the values of LFL cited in the U.S. Coast Guard's Hazard Assessment Computer System (HACS) for combustible substances in the "CHRIS Phase I" list of 400 high-priority hazardous substances (Column I). Using vapor pressure values obtained from the same source (HACS), we calculated equilibrium vapor concentrations at 40°C for 188 of the substances for which data were available (Column V). LFL-warning was considered to be necessary for all substances whose Column V values exceeded the LFL's in Column X.

It seems reasonable to assume that substances that do not produce this much vapor under anticipated ambient conditions $(-40\,^{\circ}\text{C}$ to $+40\,^{\circ}\text{C})$ will not create flammable atmospheres. It should be noted that published values for flammable limits for different substances vary over a relatively narrow range (from about 0.5-5.0% by volume in air), and that a detector whose alarm threshold can be set to respond at the

The expressions "Lower Flammable Limit" and "Lower Explosive Limit", abbreviated "LFL" and "LEL", are essentially identical in meaning and are used interchangeably.

Lable 1

Acailability of Personnel Monitoring Devices and/or leadnolygy for GRIS substances

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	71.7 (ppr)	10			3(c)	5,000		20			1,000		90		2	1	0.015		25	1	100				5				40	0.0627	
	TEME (sec.)	300		1,800	1,200			1,800			1,800				1,800		1,800		1,800	1,800	1,800				1,800						
	INHALCONC (ppm)	07		150	5			07			1,000				2		0.061		100	100	200				20						
	(Ppr.)		10,000		1,000			200			1,000				150	300			200						100				005		
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	CHEMICAL NAME	Acetic Acid	Acetaldehyde	n-Amylalcohol	Acetic Anhydride	Acetylene	Aluminum Chloride	Acrylonitrile	Acetophenone	Acrylic acid	Acetone	Acetone Cyanohydrin	Adiponitrile	Amino ethanolamine	Allyl alcohol	Allyl chloride	Aldrin	Aluminum fluoride	Ammonia, anhydrous	Ammonium hydroxide	Amyl acetate	Ammonium nitrate	Ammonium perchlorate	Ammonium sulfate	Aniline	Asphalt Blending Stocks Roofer Flux	Asphalt	Asphalt Blending Stocks Straight Run Residue	Acetonitrile	Antimony trifluoride	iso-Butvraldehyde
	CHRIS	AAC	AND	AMN	ACA	ACE	ACL	ACN	ACP	ACR	ACT	ACY	ADN	AEA	ALA	ALC	ALD	ALF	AMA	AMH	AM	AND	AMP	AMS	ANL	ARF	ASP	ASR	ATN	ATT	BAD

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	APPLICABLE DETECTOR	1	1	2	1		1							none	2	1		1	1				none					(2)			none			2	none		(2)
	LFL (ppm)	1.90 × 10 ⁴	1.40 × 104	1.70 × 104	2.35 × 104	1.70 × 104	2.00 × 10 ⁴				1.30 × 10 ⁴				1.70 × 104	1.40 × 104		1.60 × 104	2.50 × 10 ⁴		1.80 × 104		1.20 × 104					1.30 × 104	1.70 × 104					1.10 × 104			
	(ppm)		100	150	100	150	1,000		0.0385		2			0.1	200						200						2	20		0.5	10			20	0.5	0.02	89
	TIME (sec.)		1,800		1,800	1,800					1,800			1,800		1,800											1,800	1,800			1,800						
	(PPB)		150		150	300					7.5			7.0		1,000											7	100			. 25						
	(ppm)		8,000	150	8,000	10,000					3,000			10									10					200			300						
VAPOR	40°C (ppm)	3.32 × 104	2.31 × 10 ⁴	5.90 × 104	1.34 × 10 ⁵	3.71 × 10"	100	77		9.35 x 104	2.41 × 10 ⁵			5.21 × 10 ⁵	7.24 × 104	1.64 x 10 ⁴		106	4.20 × 10 ⁵	777	106		1.97 × 10 ³	3.02 × 10 ³				8.11 × 10 ⁵	2.68 × 10 ³		2.94 × 10 ⁵			5.51 × 10 ⁴	100		3.14 × 10"
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	CHEMICAL NAME	1so-Butyl acrylate	n-Butyl alcohol	sec-Butyl alcohol	tert-Butyl alcohol	n-Butyl acetate	Butadiene, inhibited	1,4-Butanediol	Benzene hexachloride	tert-Butyl hydroperoxide	Benzene	Bisphenol A	Barium carbonate	Browine	sec-Butyl acetate	n-Butyl Acrylate	1,4-Butynediol	Butylene	n-Butyraldehyde	1,4-Butenediol	Butane	Benzoic acid	Benzoyl chloride	Benzaldehyde	Calcium fluoride	Calcium hydroxide	Calcium oxide	Carbon disulfide	Carbolic oil	Cyanogen bromide	Carbon tetrachloride	Carbaryl	Calcium carbide	Cyclohexanone	Cyanogen chloride	Cadmium chloride	Cyclohexylamine
	CHRIS	BAI	BAN	BAS	BAT	BCN	108	800	ВСН	BHP	BNZ	BPA	BRC	BRX	BTA	BTC	BTD	BTN	BTR	BUD	BUT	BZA	BZC	BZD	CAF	САН	CAO	CBB	CBO	CBR	CBT	CBY	CCB	ССН	CCL	CDC	CHA

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	LFL (ppm)	3.80 x 10		1.33 × 10 ⁴						1.30 x 10							2.10 × 10	0.90 × 10	1.80 × 10			0.80 × 10	9.00 × 10 ³	2.20 × 10 ⁴				12.0 x 10 ²					1.60 × 10 ⁴		4	1.60 × 10	1.80 × 10
	(nga)	2	50	300		-				7.5	(5) (c)	50	5				C1	90	20					50(c)	7.5		1,000	200								100	25
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	(ppm)		3,500	10,000		30				2,400	1,000	250					125	8,000	2,100					1,700	1,000		50,000										2,000
VAPOR	40°C (ppm)	2.49 × 10 ⁴	9.79 x 103	2.36×10^{3}		106				3.76 × 10	4.87 × 10 ³	2.60 × 10 ³	2.69 × 10 ⁵				1.05 × 10 ⁵	3.41 × 10	5.07 × 10 ³	2.61×10^3	45	4.42 × 10 ³	1.17×10^{2}	4.93 × 10 ³		4.96 × 10 ³		106		830	75		2.5	3.84 × 103	3.14 × 104	1.5	5.72 × 10'
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18	CHRIS	CHO	CHN	CHX	CHY	CLX	CAS	CPO	CPS	CRB	CRF	CRS	CSA	CSF	css	CSY	CTA	CCS	DAA	DAL	DAN	DBC	DBL	DBO	DBP	DCE	DCF	DCM	DCP	DDC	DDN	TOO	DEA	DEB	DEC	DEC.	1.10

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APPLICABLE DETECTOR (2)		1	g j	S	e										
10.7 10.4	⁷ 01	70 70 70	× 10.	10,401	70 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0										
(ppm)	1.85 × 10 ⁴ 1.70 × 10 ⁴	1.80°x 10 ⁴ 3.20 x 10 ⁴ 1.10 x 10 ⁴	2.50 ×	3.00 × 10 ⁴ 3.80 × 10 ⁴ 2.20 × 10 ⁴ 1.00 × 10 ⁴ 2.30 × 10 ⁴	2, 90 × 10 ⁵ 1, 30 × 10 ⁵ 1, 75 × 10 ⁶ 1, 10 × 10 ⁵ 1, 10 × 10 ⁵										
11.V (ppg) 0,358	001	100	า	50 400 100	1,900										
11M17	1.800			1,800	5:0										
Coppe	ę.			200 10 000 200	<u>د</u> <u>د</u>										
(Appro)	1.000			1,000											
(mdd) (mdd)	2,500	200	4.340	300 250 10,000 2,000	250										
98 SURI (PPM) (-10 ²	x x 10, x	70 × 10 ×	to1 ,	× × × × × 10 ⁵ × × × × 10 ⁵	e <u>e e e</u> .										
VAPOR PRESSURI AU'C (ppm) 3.63 x 10 ² 2.04 x 10 ³	106 7.60 × 10 ³	1.79 x 410 3.02 x	1.10 × 10 ³	10 ⁵ 5.32 × 10 ³ 4.98 × 10 ⁴ 2.39 × 10 ⁵ 2.32 × 10 ⁵ 2.40	25 106 3.19 × 105 1.08 × 104 7.63 × 104 7.63 × 105										
SETPETION STATES IN THE SET OF	<u></u>														
CHEMICA CLASS (Sec Lable, 2) 2 2 2 2		io io io «													
CHENIC CLASS (See Lable,	~ **		in m	6 19 El 6 El	10 00 12 13 14 15 15 15 15 15 15 15 15 15 15 15 15 15										
CHEMICAL XXVII. Ethylene dibromide Ethylene dichloride Ethylenediamine tetracetic acid	Ethyl ether Ethylene glycol, none ethyl ether acetate Ethylene glycol dimethyl ether	Ethylene Elycol, Rono ethyl ethor Ethylene glycol Ethylene glycol, mono buryl ether Ethyl heweltallate	2-Ethyl hexinol Ethylene Elycol, mon methyl ether Ethoxylated dodecanol	Ethoxylated pentadecanol Ethoxylated tetradecanol Ethylene oxide 2-Ethyl-3-propylacrolvin Epichlorhydrin Ethyl acetate Ethylenecynohydrin Ethylenecynohydrin Ethoxylated tridecanol	Ethoxytriglycol Ethane Ethyleneimine Ethylene Epoxidized Vegetable O Furfural Formic acid Formaldehyde (solution)										
CHRIS CODE EDB	EGA	EGE EGE	EHX E00	EOP EOT EOX EPA EPA ETA ETA ETC ETC ETC ETC	ETT										

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	APPLICABLE TECHNOLOGY	3.9	-	-	-			1	1	-	1	1	7.9	7	6.7	1	2,7		7.9			6	5,8	8		5,8	æ	o c		5	2	3	3	1
	APPLICABLE OFTECTOR	none											none	(2),(3)	none	2,3.6	none		none			none	1			1	1	. 2		1	-	1	-	-
	(bbb)		1.10 x 10 ⁴	1.40 x 10 ⁴	1.20 x 104			1.30 x 10	6.00 × 104	1.30 × 104	1.10 x 104	1.30 × 10		5.60 × 10 [±]		4.30 × 10	7.70 × 104			0.70 × 10*			1.00 × 10 ⁴	1.00 × 10		1.20 × 104	1.20 × 104	1.20 × 104	1.20 × 104	1.20 × 10	1.80 × 10	1.60 × 10°	2.40 × 104	1.80 × 10 ⁴
	(mda)	-				25							5	10	3 (c)	10	-	3	3			-1	200			200	200	7.5		100	250	100	150	1,000
	(366.)		1.800	1.800	008.1			1.800		1,800	1,800	1,800		1,800	300																			
	(ppm)		900	500	200			200		200	.005	200		20	•																			
	1 m H (LTPm)	25												20	100	300	80		30			7.5	5,000			2,000				8,000	16,000	8,000	7.500	
VAPOR	(mdd) 5,00°	100					1.5						6.03 × 10 ⁵	1.68 x 10 ⁵	106	,01	4.34 × 10 ⁴		106	755	2.42 × 104	2.13 × 10 ⁴	1.22 × 10 ⁵	1.47×10^{5}	1.72×10^{3}	3.68 × 10 ²	4.44 × 10 ⁵	485	5.45 × 104	1.20×10^4	1.41 × 104	4.02 × 104	5.07 × 104	· 61
	SHIPPIN	1		-		-		1		_	1	7	1	1	. 1	7	1	7	1	1	S	T	7	T	1	ľ	1	1	٦.		2	1		_
CHESTICAL	(See	5.3	:1	::	21	x	'n	:	22	:1	22	22	23	23	.23	23	T,	23	23	10	10	23	-	1	4	1	1	5	7	7	80	4	oc	-
	CHEMICAL NAME	Fluorine	Gasoline Slending Stocks Mkylates	Gasolines: Automotive	Gasolines: Aviation	Glycidyl "ethacrylate	digerine	Gasolines: Casing bend	Gas oil: Cracked	Gasolines: Polymer	Gasoline Blending Stocks: Reformates	Gasolines: Straight Run	Hydrochleric acid	Hydrogen cyanide	Hydrogen chloride	Hydrogen sulfide	Hydrazine	Hydrofluoric acid	Hydrogen fluoride	Hexame thylenediamine	Hexame thylenetetramine	Hydrogen peroxide	Heptane	1-Heptene	Heptano!	Hexane	1-Hexene	Hexylene glycol	Hexanol	Isoamyl alcohol	Isopropyl acetate	Isobutyl alcohol	Isobutyl acetate	Isobutylene
	CHRIS	FXX	CAK	CAT	CAV	CCM	CCR	er.s	200	GPL	GRF	GSR	HCL	HCX	HDC	HDS	HDZ	HFA	HFX	HOD	HMT	HPO	HPT	HTE	HIN	HXA	HXE	HXC	HXN	IAA	IAC	IAL	IBA	IBL

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	BLE	1													I	BON	OOK.	X .												7					
	APPLICABLE TECHNOLOGY						5.7														1				5.7	5,7	5,9	1	•	5, 8,				8.8	5.8
	APPLICABLE DETECTOR	1		1			•	-	1		2	2	2	2						1	1		1	1	. 1	1	(2)	4	1	1				1	
	LF1 (ppm)	1.80 × 104	1, m = 18	1.20 x 10 ⁴	0.90 × 10 ⁴		2.00 × 10 ⁴	2.00 x 10 ⁴	1.40 × 104		1.30 x 10	0.70 × 10 ⁴		0.60 × 104	0.70 × 10 ⁴					5.30 × 10 ⁴	1.80 × 10 ⁴		1.00 × 104	0.90 × 104	6.00 × 104	2.80×10^4				1.80 × 104	1.10 × 104			1.00 × 104	1.40 × 10
	VIIA (Film)						700				200	200	200	200	700			0.0097			1,000		25		500	10	1,000	0.0056	3	200				72	100
	1114																									1,800									
	(ppm)																									25									
	(ppr.)						2,000											3,000			19,000				25,000	1,000		3	1,000	3,000				2,000	
: Alor	(mdd) 3,00+	106	2.01 × 10 ³	5.00 × 103	1.46 × 10	1.45 x 10 ³	1. 48 × 10 ³	901	10و	2.01 × 10.5	1.96 × 10 ⁵	7.52 × 10 ³	4.83 × 10 ⁵	3.43 × 10 ³	7.52 x 10 ³					106	106	245	2.11 × 10 ⁴	3.69 × 10 ⁴	3.38×10^{5}	2.72 × 10 ³	106	7.95	1.73×10^{3}	2.35×10^{5}	7.97×10^{3}		9.42 × 10	2.11×10^4	5.76 × 104
	STIPTING	-			-	I.	L	-		ı	Г	1	7	_1	ı	s	1	s	1	T	T	r	1	r	Г	r	Г	Г	T	1	1	•	۵		4
CLASS	(see	-	4	-	•	٤	.,	-	-	.,	22	22	22	22	22	23	٠,7	23	22	22	22	12	4	80	7	80	e 2	23	10	9	21		23	4	•
	CHEMICAL NAME	Isobutane	Isodecaldehyde	Isohexane	Isooctyl alcohol	Isooctaldehyde	Isopropyl alcohol	Isoprene	Isopentane	Isodecyl alcohol	Jet fuels: JP-1	Jet fuels: .IP-1	Jet fuels: JP-3	Jet fuels: JP-5	Kerosene	Lithium aluminum hydride	Linear Alcohols (12-15 carbons)	Lead arsenate	Latex, liquid synthetic	Liquified natural gas	Liquified petroleum gas	Lauryl mercaptan	Methyl amyl alcohol	Methyl amyl acetate	Methyl alcohol	Methyl acrylate	Monochlorodifluoromethane	Mercury	Monoethanolamine	Methyl ethyl ketone	Methylethyl pyridine	Motor fuel anti-knock	lead alkyls	Methyl isobutyl carbinol	Methyl isobutyl ketone
	CHRIS	181	IDA	THA	104	100	IPA	IPR	IPI	15A	JPF	ogr Ogr	JPI	VAL	KRS	LAH	TY.	LAR	LLS	LNG	LPG	LRM	MAA	MAC	MAL	MAM	MCF	MCR	MEA	MEK	MEP	MFA		MIC	MIK

		CHEMICA		VANOR					•		
CHRIS		esec.	SHEEPING	AT	IDITH	I VHALCONG	17	7.11.7	11	APPLICABLE	APPLICABLE
CODE	CHEMICAL NAME	Cable 2)	STATE	(mdd) no.	(अंग्रेस)	()	(sec.)	(((((((((((((((((((((mdd)	DETECTOR	IF CHNOLOGY
MLA	Maleic anhydride	1	s					0.25	1.40 × 10		
MLT	Malathion	97	-	The second second	. 140			0.68			
MOCH	Methyl methacrylate	v.	1	.1.07 x 103	7,000			100	2.10 x 104	1	7
SINS	Mineral spirits	27	T.	9.42 × 10				200	0.80 × 10 ⁴	7	5.7
MF.A	Monoisopropanolamine	10	L	3,45 x 10 ³				.5	2.20 × 10 ⁴	none	œ
MPL	Morpholine	10	1	4.14 × 10 ⁴	8,000			20	1.80 × 10 ⁴	-	•
MPT	Methyl parathion	79	r					001			
MSA	Methane arsonic acid, sodium salts	39	7				v				•
NT.B	Methyl bromide	, r.i	1	106	2,000			20(c)	20(c) 10.0 x 10 ⁴	1	5.7
MIC	Methyl chloride	. 2	7	106	10,000			100	8.10 × 10 ⁴	-	5.7.9
HIK	Methane	1	7	100					5.00 × 10 ⁴	1	
NAC	Nitric acid	23	1		100	15	300			non	7
NCT	Naphtha: coal tar	22	1	9.42 × 103	10,000			100		1	5,7
NKS	Nickel sulfate	23	s					0.145			34
IKN	Nitromethane	16	7	9.51 × 10 ⁴	1.000			100	7.30 × 104	1	2.5
NNE	1-Nonene	1	. 1	1.68 × 10					0.80 × 104	•1	
NNN	Nonanol	• 1	1	140					0.80 × 10		
NNP	Nonylphenol	17		1.4					1.00 × 10		
NON	Nonene	1	Т	1.70 × 10					0.70 × 10	1	
NOX	Nitrogen tetroxide	23	T	106	20	25	300			none	,
NSS	Naphtha: stoddard solvent 22	1t 22	1	9.42 x 10 ³	2,000	200	1,800	200	0.80 × 10		5.7
NSN	Naphtha: solvent	22	7	9.42 x 10 ³		200	1,800	200	0.80 × 10	1	5,7
NTB	Nitrobenzene	16	1	955	200	. 01	1,800	1	1.80 × 10 ⁴	2	5,8
NTC	Nitrosyl chloride	23	Г	106				1		none	6
KIN	Naphtha: molten	20	S	780		15	300	10	0.90 × 104	7	7.8
NVM	Naphtha: VM6P	22	1	9.42 x 10 ³		200	1,800		0.90 × 104	1	7,8
OAS	Oils, miscellaneous: absorption	22	. 1	7.59 x 10 ³							
OCA	Oils, edible: castor	22	L	7.50×10^{3}		,					
OCF	Oils, clarified	22		7.59 x 10 ³							
SOO	Oils, edible: cottonseed	1 22	1	7.50×10^{3}							
OCT	Oils, miscellaneous:	22	T	7.59 x 10 ³					1.30 × 10 ⁴	1	
SOO	Oils: diesel	22	-	7.69 × 103					1.30 × 104	-	
OFR	011s, fuel: No. 4	22	2	7.59 × 10 ³					1.0 × 104		
OFS	Oils, edible: fish	7.7	ı	7.50 × 10 ³							

		CHEMICAL. CLASS		VAPOR PRESSURE							
CODE	CHEMICAL NAME	(see Table 2)	SHIPPING	AT 40°C (ppm)	(mdd)	(bba.)	() () () () () () () () () ()	(bpm)	(mdd)	APPLICABLE DETECTOR	APPLICABLE TECHNOLOGY
OFV	Oils, fuel: No. 5	2.2	٠	7.59 x 10 ³					1.00 × 10 ⁴	-	
OIL	Oils: crude	22	د	7.59 × 10							
870	Oils, miscellaneous: lubricating	23	1	7.59 x 10 ³							
MIO	Oleum	33	ı				300				
ONIN	Oils, miscellaneous: mineral	22		7.59 x 10 ⁴							
OMS	Oils, miscellaneous: mineral seal	::	2	7.59 × 10³)	200		٠.	5.5
OMT	Oils, miscellaneous: motor	21	1	7.59 x 10 ³							
ONF	Oils, miscellaneous: neatsfoot	22	_	7.59 x 10 ³							
000	Oils, fuel: No. 1-D	22	ľ	7.52 × 10 ³					1.30 x 10 ⁴		5,7
OOL	Oils, edible: olive	22	1	7.50 x 10 ³							
X00	Oils, fuel: No. 1	13		7.52 × 10 ⁵				200	0.70 x 10*		5.7
NAO	Oils, edible: peanut	7.7	-	7.50 x 10							
OPT	Oils, miscellaneous: penetrating	22	J	7.59 × 10 ³							
O.K.O	Oils, miscellaneous: road	22	ľ	7.59 x 10 ³							
ORG	Oils, miscellaneous:	22	ח	7.59 x 10 ³				200	0.70 × 10	a	5.7
ORN	Oils, miscellaneous: rosin	22	٦.	7.59 x 10 ³							
ORS	Oils, miscellaneous: resin	22	L	7.59 x 10 ³							
OSB	Oils, edible: soya bean	22	T	7.50×10^{3}							
OSD	Oils, miscellaneous: spindle	22	- 12	7.59 x 10 ³							
OSP	Oils, miscellaneous:	22	ů.	7.59 x 10 ³							
XSO	Oils, fuel: No. 6	22	ľ	7.59×10^{3}					1.00 × 10 ⁺		
OSY	Oils, miscellaneous: spray	22	נו	7.59 x 10 ³				200	0.60 × 10 ²	r I	5.7
OTA	Octanol	7	ľ	410							
OTD	Oils, fuel: No. 2-D	22	1.	7.59 × 10 ³					1.30 × 10		
OTE	1-Octene	1	T.	4.99 × 104					0.90 × 10		5,7
OTF	Oils, miscellaneous: transformer	22	-	7.59 × 10 ³							

				THI	ST	AG	et	S B	5 53	g QI	JAL	IT'	Y P	RAG	TI	4	Į.																	
	APPLICABLE TECHNOLOGY			FRA	. AL.	,	1 .	- 	5,7,8									5,9	7.9		•	ix:	10			a. r.	7.9			7.9		e	7.4	7.3
	APPLICABLE DETECTOR							1	1	1	1							(2)	rı.		•	none	٠,			1	none			none		1	-	-
	LFL (ppm)							2.60 × 10	2.10 x 10 ⁶	1.70 × 10 [±]	2.00 × 10 ⁴					0.70 × 10			1.70 x 10 ⁴			2.90 × 10 ⁴	2.10 x 10 ⁴		2.60 × 10 ⁴	2.00 × 104						1.80 × 104	2.10 × 104	1.40 × 104
	LLV (blue)								200	7	200			0.042				0.1	\$		100	10	100			000.4	0.5	10		0.5	0.018	\$	000'1	200
	rine (sec.)								008.1	004								300										300						
	INHAI CONC								700	.1								1										20						
	(mid)					125			7,000	1,500	8,000			13				-1	250									75		20		3,600	20,000	15,000
VAPOR	N Doot	7.30 x 103	7.59 x 10 ³	7.59 x 10 ³	7.50 × 10 ³			7.49 x 103	5.67 × 10	43	9.34 × 10 ⁴				0.055			106	2.68 × 10 ³	70	3.46 × 10 ⁴	1.38 × 10 ⁴	106	0.0002	430	106	9.23×10^4			3.07 × 10 ⁵		5.94 × 10 ⁴	g01	.01
	SHIPPING	_	1	-1		×	1	7			Γ		7	s.		s		. 1	1	T	J.	Γ	Г		T	r	Г	S	S	L	S	Τ.	1	1
CHEMICY	(Sec Table 2)	81	:1	77	:1		7.3	£	.1		80	mer 1	1 15	18	.1	¥	2	23	17	1	5	1	5	23	. 5	1	23	23	23	23	23	21	-	1
	CHEMICAL NAME	Oils, miscellaneous: tall	Oils, missellameeus: tammers	Oils, fuel: No. 2	Oils, edible: vegetable	Oxalic neid	Phosphoric acid	Propionaldehyde	n-Propyl alcohol	Phthalic anhydride	n-Propyl acetate	Propylene butylene polymer l	Polychlorinated biphenyl	Pentachlorophenol	Pentadecanol	Paraformaldehyde	Polypropylene glycol	Phosgene	Phenol	Polybutene	Propylene glycol methyl ether	Propionic acid	Propylene oxide	Polyphosphoric acid	Propylene glycol	Propylene	Phosphorus oxychloride	Phosphorus pentasulfide	Phosphorus, red	Phosphorus trichloride	Phosphorus, white	Pyridine	Propane	Pentane
	CHRIS	OTL	OTN	OTW	OVG	OXA	PAC	OK.	PAL	PAN	PAT	PBP	PCB	PCP	PDC	PFA	PGM	PHG	PHN	PBL	PME	PNA	POX	PPA	PPG	PPL	PPO	PPP	PPR	PPT	PPW	PRD	PRP	PTA

	APPLICABLE TECHNOLOGY							5.7		6																					6					5,7,8	
	APPLICABLE DETECTOR			1				1		2																					none				SANTA SANTA	1	
	(ppm)			1.40 × 106				0.90 × 104																												1.10 × 10 ⁴	
	TLV (PPm)									200																	0.229		2		-					100	
	(sec.)							1,800																			300		300								
	(ppm)							200																			2.29		20								
	(Ppm)							10,000																			18		100		10					2,000	
VAPOR PRESSURE	40°C (Ppm)			106				9.42 × 10 ³		5.74 × 10 ³									3.40 × 10 ⁵						٠				106		3.73 × 10 ⁴				The state of the s	1.94 × 104	
	TE	S	S	L 10 ^b	S	S		L 9.42 x 10 ³	S	L 5.74 x 10 ³	L			S			S		L 3.40 × 10 ⁵	S	S	8	S		S	S	7	S	1. 106		×	-	S	-	8	1.94 × 104	× .
	SHIPPING STATE					23 S								23 S	13	23	. 23 S.				23 S	23 S	23 S	23	23 S	23 S	23 L			55	3.73 ×		23 S	23 L			23 S
	(see SHIPPING Table 2) STATE	23	S		S		٠	u	S		7	1-benzene	E ;		Sodium alkylsulfates 13	Sodium borohydride 23		1	7	S				Sodium hydride 23				S	L	1. 55	L 3.73 ×	2			S	14 1.	

	APPL ICABLE		7.8.9	. 6	2,3,7,5			80					80	5,7		5,7	80			8	5,7				3,9									6.8	3,7,8,9,5	
	APPLICABLE		2	none	1			63					none	1		1	(2)		1	none	1	•	1		2								none	none	2	
	LFL (ppm)	/	7.00 × 104		8.00 × 104			0.02(c) 0.90 x 104						1.20 × 104		1.80 × 10 ⁴	0.80 x 10 ⁴		2.00 × 10 ⁴		1.27 × 10 ⁴		0.80 × 10 ⁴										2.60 × 10 ⁴	7.30 x 104	4.00 × 104	
	TLV (pom)		350	1,000	100			0.02(c)					0.1	25		200	25			0.013	100		100		100								10	25	200	
	TIME (Sec.)				1,800									1,800		1,800					1,800		1,800												300	
	INHALCONC (ppm)				200									100		200					009		200												200	
	IDLH (ppm)				1,000			10					2.8	1,000		20,000				3.3	2,000		1,900		200			10								
VAPOR	PRESSURE AT 40°C (ppm)	0.29	3.08 × 10 ⁵	901	1.83 × 10 ⁵	0.65	205	06	1.5	0.04	2.34 x 10 ³	0.81	1.13 × 10 ⁵	1.74 × 10 ⁵	8.4	3.91 × 10 ⁵	1.90 × 10 ³		106	8.96 × 10 ⁴	7.79 × 10 ⁴		1.97 × 10 ⁴	09	5.53 × 104	405	4.16 × 10 ⁴		1.92×10^3	17.5		9.49 × 104	2.97 × 10 ⁵	106	106	
	SHIPPING	-3	1	_	1	1	٦	د	1	1	-1	٠.	1	1	7	٦	_1	. 1	1	r	. 1	S	1	.1	1	Г	Г	s	. 1	Г	s	7	_1	Г	7	
CHEMICAL	CLASS (see Table 2)	23	2	2		56	1	6	-7	10	14	5	23	10	10	2.7	20	. 22	10	23	14	18	22	1	2	7	23	15	1	. 7	80	9	80	2	2	
	CHEMICAL NAVE	Sulfur (liquid)	Trichloroethane	Trichlorofluoromethane	Trichloroethylene	Tricresyl phosphate	1-Tridecene	Toluene-2,4-Diisocyanate	Tridecanol	Triethanolamine	Triethylbenzene	Triethylene glycol	Tetraethyl lead	Triethylamine	Triethylenetetramine	Tetrahydrofuran	Tetrahydronaphthalene	Tallow	Trimethylamine	Tetramethyl lead	Toluene	Trichlorophenol	Turpentine	1-Tetradecene	Tetrachloroethylene	Tetradecanol	Titanium tetrachloride	Toxaphene	1-Undecene	Undecanol	Urea	Valeraldehyde	Vinyl acetate	Vinylidene chloride (inhibited)	Vinyl chloride	
	CHEIS	SXX	TCE	TCF	TCL.	TCP	TDC	TDI	TOX	TEA	TES	TEG	TEL	TEN	TET	THE	THIV	ILO	THA	TMT	TOL	TPH	TPT	TTD	TTE	. XII	TIT	TXP	. DQD	UND	URE	VAL	VAM	VCT	VCM	

APPLICABLE TECHNOLOGY (2).8 5,7.8 5,7.8 5,7.8	
API 150	
w 1 : salabas da 11sala	
APPLICABLE DETECTOR 1 1 1 1	And a country of the
1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	
A - 1	
40 40 40	
(ppm) .80 × 1 .10 × 1 .10 × 1	
1.FL (ppm) 0.80 × 10 ⁴ 1.10 × 10 ⁴ 1.10 × 10 ⁴	
	when the role and to the label of the label of the
11.V (PPm) 100 100 100 100	
300 300 1,800 1,800	
	The second secon
SNC C	
(ppm) 400 300 300	
NI CONTRACTOR OF THE CONTRACTO	
0 000	
(Ppm) 5,000 1,000 1,000	
00 00 00 00 00 00 00 00 00 00 00 00 00	
VAPOR AT AT AT 5.25 x 10 5.25 x 10 6.25 x 10 7.49 x 10 7.01 x 10 7.62 x 10	
VAPOR PRESSURF AT 40°C (ppm) 5.25 x 10 ³ 5.25 x 10 ⁴ 2.49 x 10 ⁴ 2.01 x 10 ⁴ 2.62 x 10	
SHIPPING STATE L L L L L L	
STAIL STAIL STAIL STAIL STAIL S	
8	
7 2	A SECOND
CHEMICAL CLASS (See Eable 2) 14 22 22 22 14 14 14	
8 5 3 E	
	The second secon
CHEMICAL MANE Vinyl toluene Waxes: carnauba Waxes: paraffin m-Xylene o-Xylene P-Xylene Zinc chloride	
CHEMICAL MANE Vinyl toluene Waxes: carnaub Waxes: paraffi m-Xylene o-Xylene P-Xylene Zinc chloride	
CHEMICAL Vinyl to Waxes: ce Waxes: pe Waxes: pe Waxes: pe Waxes: pe Co-Xylene P-Xylene Zinc chld	
Vin Wax Wax m-X o-N Zin	
v.	
CHRIS CODE WCA WPF XLM XLM XLM XLM ZCH	33

appropriate point in this range will not be greatly in error if the composition of flammable substances changes somewhat for any unforeseen reason. Thus, while it may be important to know what the principal flammable substance may be in any particular instance, the presence of minor quantities of other combustibles is not likely to require a change in the alarm level.

b. Toxicity Sensor

The toxicity sensor should be capable of detecting all CHRIS chemicals that can exist in the vapor phase at 40°C at concentrations immediately dangerous to life and health.

Since all 900 of the chemical substances listed in CHRIS (with a few exceptions such as dextrose solution, sucrose solution, and corn syrup) are potentially toxic, either by inhalation, by skin contact or by direct ingestion, it is important to be able to detect the presence of any of them that can penetrate the protective air filter. Since some CHRIS substances have vapor pressures so low that they exist only as particulates, while others would form appreciable vapor concentrations in air at 40°C, a division of CHRIS substances into particulate contaminants and vapor contaminants has been made and is shown in Appendix C, Tables C-1, C-2 and C-3. Table C-1 lists CHRIS compounds whose vapors readily penetrate the XM-41 Filters, and against which it is not considered to provide satisfactory protection. Table C-2 lists those substances whose vapor pressures are sufficiently low that only very small concentrations can occur at 40°C, and which are therefore retained satisfactorily by the filter. Table C-3 includes particulate solids and liquids which are effectively retained by the filter. No vapor-phase monitoring is presumed to be required for substances in Tables C-2 and C-3.

Since the CHRIS manuals were developed in three stages over a period of several years, it was found necessary to identify at the outset those substances requiring earliest consideration because of their specially hazardous nature. "CHRIS Phase I" identified 400 chemicals judged to be most important to Coast Guard response personnel. The list of chemicals includes all of the 284 materials in 46 CFR 151, Cargoes Regulated by Subchapter 0 (Table 151.01-10b) and Cargoes Regulated by Subchapter D (Table 151.01.10d). The remainder of the chemicals were selected from a preliminary list of Hazardous Polluting Substances that had been prepared by the EPA. Selection of chemicals from this list was based on experienced judgment as to the chemicals where CHRIS data may be most important. This selection was made by the consensus of several knowledgeable professionals on the basis of relative magnitude of quantities of the chemical being shipped, the extent to which the chemical may be transported and its hazard severity. The selected list was reviewed, discussed, and approved by the Coast Guard.

The 400 "CHRIS Phase I" chemicals include those materials commonly shipped in bulk along with substances which create special hazards during shipment. Since these substances are most likely to be encountered in hazardous situations, they deserve first priority in the Coast Guard's efforts to develop personnel monitoring systems.

While the substances identified in Table C-1 might be considered a suitable subcategory for evaluation of toxic vapor monitors, the CHRIS Phase I list was judged to be of at least equal significance, and, furthermore, to contain most of the substances for which IDLH and vapor pressure values were obtainable from HACS. For this reason, Table 1 was used as the basis for this evaluation. Few substances of major concern (carbon monoxide is one of them) are absent from the CHRIS Phase I list, and these have been identified and added to the list. Another group of substances which should not be overlooked is that represented by reaction products of hydrolysis, combustion, etc., which may be toxic but not included in the entire CHRIS list. Comparison of CHRIS against other lists of known toxic substances should eventually be made.

Table 1 contains the 400 "CHRIS Phase I" substances arranged in alphabetical order according to their codes, which are shown in Column I. The accepted chemical name of each substance is given in Column II. In Column III are the numbers of the chemical classes, listed in Table 2, to which the substances have been assigned for the purposes of the present task. Column IV shows the usual physical state in which the substance is shipped, either solid or liquid, and in Column V the equilibrium vapor concentrations calculated at 40°C (the maximum temperature the Coast Guard would allow its personnel to work in) are listed. Vapor pressure data were obtained from the U.S. Coast Guard's Hazard Assessment Computer System (HACS).

To determine which of the CHRIS Phase I compounds would present a hazard to people working in atmospheres in which these vapors were present, the vapor concentration can be compared with several values which outline varying degrees of danger. The first, listed in Column VI of Table 1, is the IDLH.

Federal regulations (30 CFR 11) concerning the use of respiratory protective equipment make a distinction between devices which may be used under conditions immediately dangerous to life or health (IDLH) and devices which (due to lower reliability) may be employed only in less hazardous environment.

The definition of IDLH provided in 30 CFR 11.3(5) is:

"Immediately dangerous to life or health means conditions that pose an immediate threat to life or health or conditions that pose an immediate threat of severe exposure to contaminants, such as radioactive materials, which are likely to have adverse cumulative or delayed effects on health."

Table 2
Chemical Categories of CHRIS Substances

Category Number	Applicable Detector Principle (5)* for IDLH Monitoring	Chemical Classification
1	(1),2,3,5,7,8	Aliphatic Hydrocarbons: Alkanes, Cyclic Alkanes, Alkenes, Cyclic Alkenes Dienes and Alkynes
2	(1),2,3,5,(7),8,9	Alkyl Halides: Saturated and Unsaturated
3	(1),2,3,5,(7),8	Ethers: Aliphatic, Aromatic and Cyclic
4	(1),2,3,5,(7),8	Alcohols
5	(1),2,3,5,(7),8	Glycols and Epoxides
6	(1),2,3,5,(7),8	Aldehydes and Ketones
7	(1),2,3,5,(7),8	Carboxylic Acids and Anhydrides
8	(1),2,3,5,(7),8	Esters and Amides
9	(1),2,3,5,7,8	Nitriles and Isocyanates
10	(1),2,3,5,(7),8	Amines and Imines; Aliphatic and Aromatic
11	(1),2,3,5,(7),8	Hydrazines
12	(1),2,3,5,(6),(7),8	Alkyl Sulfur Compounds
13	3,7,(8)	Sulfonic Acids, Sulfoxides
14	(1),2,3,(4),5,7,8	Aromatic Hydrocarbons
15	(1),2,3,(4),5,7,8,9	Halogenated Aromatic Compounds
16	(1),2,3,(4),5,7,8	Aliphatic and Aromatic Compounds
17	(1),2,3,(4),5,7,8	Phenols
18	(1),2,3,(4),5,7,8,9	Halogenated Phenols
19	(1),2,3,5,7,8	Nitro Phenols
20	(1),2,3,5,7,8	Fused-ring Aromatic Hydrocarbons
21	(1),2,3,5,7,8	Heterocyclic Nitrogen Compounds
22	(1),2,3,5,7,8	Mixed Hydrocarbons and Oils
23	(2),(3),(5),7,(9)	Inorganics and Organometallics
24	2,3,5,9	Halogenated Ethers
25	3,(5),(7)	Peroxides
26	2,3,7	Organophosphorus Compounds
27	(1),2,3,5,(7),8	Heterocyclic Oxygen Compounds
28	2,3,5,8	Heterocyclic Sulfur Compounds
29	2,3,5,7,8	Organoarsenic Compounds

^{*} See Table 3; Numbers in parentheses indicate partial applicability.

The purpose of establishing an IDLH exposure concentration is to ensure that the worker can escape without injury or without irreversible health effects from an IDLH concentration in the event the respiratory protective equipment fails. The IDLH is considered a maximum concentration above which only a highly reliable breathing apparatus providing maximum worker protection is permitted.

In developing guidelines for hazardous substances, the National Institute for Occupational Safety and Health (NIOSH) and the Occupational Safety and Health Administration (OSHA) have defined specific IDLH levels for 385 substances. In establishing the IDLH levels, the following two criteria were applied:

- 1. Escape without loss of life or irreversible health effects must be possible at the IDLH level. (Thirty minutes is considered the maximum permissible exposure time for escape.)
- 2. Escape must be possible at the IDLH level without severe eye or respiratory irritation or other reactions that would prevent escape without injury.

The IDLH levels defined by NIOSH and OSHA represent maximum escape concentrations for personnel exposure of thirty minutes or less. Since most Coast Guard emergency response situations may involve short-duration, high-intensity exposures, the IDLH level represents an appropriate level for evaluating hazards to response personnel.

For many compounds, the IDLH value has not yet been established. For those substances a second, generally lower, value, that of the "Inhalconc.", the short-term inhalation limit, was obtained from the HACS system. These values, given in Column VII of Table 1, are associated with time, in seconds, (Column VIII) for which a person may be exposed to the stated concentrations without suffering permanent damage. Finally, there is a much more stringent set of values, the OSHA Standard or "TLV," given in Column X, which are time-weighted averages of levels which can be expected to be safe for continuous occupational exposure.

In the event that Coast Guard personnel were required to remain in a contaminated area for several days or weeks, consideration would have to be given to the possibility of a continuous occupational exposure standard (the TLV or OSHA Standard) being more appropriate than an IDLH value. Under these circumstances, real-time response, such as would be required for an IDLH-level personal alarm, would be unnecessary, and an entirely different concept of personal monitoring would be applicable. Monitoring at the OSHA Standard or TLV level is ordinarily accomplished by the use of a personal sampling pump which draws air at a known volume rate through a filter, impinger or sorption cartridge for a fixed period of time, usually eight hours. The sampling element is then analyzed for its total "catch" of the toxic substance of concern, and the resulting

"time-weighted average" is calculated to determine the average continuous exposure level. Clearly, the use of OSHA Standard (TLV) exposure values that are designed for continuous exposure, anticipates momentary exposures that may be considerably higher than the prescribed level. Therefore, to set a real-time alarm at those levels would invoke an extremely conservative standard of protection which would be inconsistent with current practice.

A few substances have OSHA Standard concentrations that carry the designation "C", indicating a "ceiling" level. The intent of the regulation is that this level should never be exceeded, and therefore a real-time response would be appropriate for these substances at the indicated concentrations.

Values listed under "Vapor Pressure at 40° C" in Column V are given in "ppm" (parts per million by volume in air) rather than in the more customary units of mm of Hg, atmospheres, etc. to be more directly comparable with the concentrations listed in Columns VI, VII and IX. Values of "LFL" are normally given as percentages (by volume) in air. These have also been converted to "ppm" for purposes of easy comparison. (Note that 1.0×10^4 ppm = 1.0%.)

The names of 188 substances whose vapor pressures are high enough at 40°C to given concentrations in air that exceed the IDLH, or if that is not available, the "Inhalconc." or if neither are given, the TLV, or if none of these are known, the LFL, have been underscored. These substances, with the possible exception of those that exceed only the TLV, are the ones that are of principal concern to the present task, since they have vapor concentrations high enough either to be flammable in air or to penetrate the present U.S. Coast Guard personal aircleaning device at levels that present an immediate danger to the health and safety of the individual. Examination of Table 1 will reveal some apparent exceptions to the group of 188 that probably warrant concern. Unfortunately, since reliable data were not available for the entire list of 400 CHRIS substances, those for which essential data were not available could not be designated for evaluation. With few exceptions, however, these omissions are unlikely to represent severe flaws in the report, since full data for similar substances are usually given.

The current Coast Guard back pack filter is primarily effective against particulate aerosols, but it is not considered effective when challenged by most common vapors. Present Coast Guard plans call for the development of a self-contained breathing and body-cooling air supply capable of providing a two-hour service life when used in conjunction with the Coast Guard protective suit. When this self-contained breathing supply is available, the protective suit will be applicable to a much wider range of hazardous situations than is now the case. The switch from an air-purifying to a self-contained breathing system will also introduce several important changes into the performance requirements applicable to the toxicity sensor.

Most organic vapors present in any spill area will quickly penetrate the filter system of the present XM 41 back-pack filters. Since the identity and possible presence of these vapors would presumably be known beforehand, it must be assumed that the decision to enter the spill site implies that the risk of inhaling them at any concentration that is not immediately dangerous to life and health has already been determined to be acceptable. With respect to most toxic vapors, therefore, the requirement for sensitivity and selectivity of the desired monitor for use in the present protective suit must be the same as if no air-purifying system was being used at all.

When the planned self-contained air system is available for use by Coast Guard response personnel, the need for a toxicity monitor will be significantly changed. When the new system is used, there will presumably be no opportunity for the breakthrough of contaminants through a sorbent medium. Rather, the principal concern will be for leak detection. Thus, rather than monitoring external air entering the protective suit, it will probably be necessary to monitor recycled air which may carry organic contaminants produced by the body of the user (i.e., inhalation and perspiration will introduce into the protective suit system contaminants with which the sensor must cope.)

c. Protective Suit Sensor Specificity

The protective suit integrity sensor need not be specific relative to the cause of loss of suit integrity.

This requirement is self-explanatory. The sensor should be able to detect an actual loss of integrity immediately upon occurrence. Ideally, the system should also indicate an incipient loss of integrity, giving the wearer time to take remedial action before his safety is actually compromised.

6. Durability

The personnel monitor should be capable of withstanding vibration and shock, and should be operable in any physical orientation.

During normal spill response operations, Coast Guard spill response personnel are subject to vibration from moving platforms and vehicles, falling against stationary objects, and bending and stretching to conduct necessary tasks. The monitoring system must work under all of these conditions.

Power Requirements

The personnel monitor should have its own self-sufficient source of power capable of providing power for at least two hours of operation. Since this power source is self-contained, the amount of power available will be limited only by size and weight considerations.

Existing power supplies built into the Coast Guard protective suit do not have any significant amount of available excess capacity. Thus, the personnel monitor must include its own power supply. Only size and weight limit the amount of power available for the monitoring system.

8. Hazardous Materials

The operation of the monitoring systems should not introduce any new hazardous materials into the breathing environment of the user.

Because some types of detectors operate at elevated temperatures, it is important to ensure that such detectors do not cause a degradation of contaminants into new, possibly more toxic, contaminants.

9. Maintenance

The monitoring system should be packaged for transport along with the tools, instruments, chemical reference standards, etc., that are needed to perform maintenance and calibration in the field. The frequency of needed colibration during use should be no more often than every three hours, and the stability of calibration during storage and transportation should be known.

Because maintenance and calibration will be necessary in the field, it is important to assure that all needed apparatus is readily available. Since a two-hour work shift is anticipated, calibration during use must be stable for at least that amount of time, with some safety margin. Since the monitoring device may be in storage for long periods between uses, the stability of its calibration during storage must be known.

10. Complexity

The monitoring device should operate without user interaction; however, some presetting of controls is permissible so long as protocol for making such adjustments is understandable to reasonably literate persons without a special technical education. Further, maintenance and calibration of the monitoring device should be within the capabilities of persons without specific advanced training in analytical chemistry, electronics, etc.

Members of Coast Guard Strike Teams generally do not have advanced-level training in the sciences. These persons must be capable of operating and maintaining monitoring equipment during response actions. While response personnel cannot be expected to take time to actively operate an analytical instrument during their response work shifts, it is acceptable to require that some presetting of controls be associated with use of the personnel monitor.

11. Signals

The monitoring device should provide a unique, recognizable signal indication of each type of hazard of interest (flammability, toxicity, oxygen deficiency, and breech of suit). The signal should be provided without the need for inquiry of the detector by its user, and the signal should actively attract the user's attention.

Because the reaction of a response team member to oxygen ueficiency may differ from his response to the presence of a flammable atmosphere, it is important for the monitoring system to provide discreet, and recognizable warnings. Such warnings will permit appropriate assessment by response team members of their best course of action. The warning signal must be unmistakable and automatic to ensure that pre-occupation with the completion of difficult response tasks does not result in overlooking a hazard signal.

B. TASK II: SURVEY OF PERSONNEL MONITORS

1. General Observations

In our survey of existing and available personnel monitoring devices and potentially applicable technology we contacted, either by mail, by telephone or by personal visit, eighty-five (85) commercial suppliers of related supplies and equipment. These are listed in Appendix B. Our search of the technical literature produced a total of one hundred sixty-six (166) pertinent articles. These are listed in Appendix A. The bibliographic list is designated as "preliminary" to underscore the fact that the field of personnel monitoring for chemically hazardous substances is now in a process of rapid growth and development. New information is being contributed every day, and any list, no matter how exhaustive, of literature published in the past is bound to become severely out of date in a relatively short time.

Responses from manufacturers and vendors of personnel monitoring devices were surprisingly meager, given the current growth of interest in such equipment. This poor response is attributed, we believe, to a natural time-lag in the development of commercial products to meet the needs of emerging market needs. A number of small business concerns either are or have been in the market in recent years, but the field shows the type of instability characteristic of this kind of early growth condition. Presumably, a number of reliable and consistent manufacturers and vendors will emerge as time goes on.

Our results are reported here for purposes of convenience in categories organized, first by purpose of monitor (i.e., oxygen deficiency, flammable vapors, toxic vapors and suit integrity), and second by type of detection principle. A third category is devoted to existing multifunctional systems of combined monitors, a few of which are now on the marekt. Table 3 lists currently available personnel monitors and includes some devices that represent technology potentially applicable to USCG specifications, even though in their present commercial forms they may not meet all present requirements.

Oxygen Deficiency Monitors

a. Introduction

Two basic types of 0₂ deficiency detection systems are commonly available at the present time. One is the electrochemical cell which utilizes an electrochemical reaction within a sealed cell containing various electrodes and electrolytic solutions. The other operates on the principle of a galvanic cell, similar to the manner by which the common dry cell works. Both types are available from a number of different manufacturers and discussion of one particular manufacturer should not be construed as a recommendation.

Table 3

Toxic and/or Flammable Gas Detectors

MANUFACTURER	MODEL	WEIGHT, 16.	DIMENSIONS, in.	POWER/OPER. TIME	RFSPONSE TIMF, sec.	SIGNAL	SENSITIVITY	GAS/VAPORS DETECTED
CATECORY 1: CATAL	CATALYTIC OXIDATION							
Bacharach	JW-SSP	6-3/4	8 x 3 x 6	Ni-Cd/10 hrs.		Meter	0-1000 ppm	Combust (5) es
Bacharach	J-MC	4	4-3/4 x 3 x 5-3/4	D/?		Neter	0-100% LEL	Combust 151es
Bacharach	JW-Sent.		10 x 6 x 6	Lead Acid/?		Alarm	0-100% [F:	Combust 15'es
Bacharach	Barton 282	2-3/16 + batt. 2-1/8		Ni-Cd/10 hrs.		Meter +	50 ppr	Combust (b.) es
Bacharach	Barton 310	2-3/16 + batt. 2-1/8		Nf-Cd/IO hrs.	. 2	Alarm Meter + Alarm	10 ppm H2	Cumbustibles or H. orly
ERDCO	03HCS	1-3/4	8 x 1-3/4 x 3	Ni-Cd/10 hrs.	٤٠	Meter	0-100° LEL	Combustibles
ERDCO	05нсѕ	2-1/4	9 x 2-3/4 x 3-1/2	Ni-Cd/10 hrs.	7	Meter + Alarm	0-107, 0-130% LEL	Combustibles
ERDCO	06нся	,	6-3/4 x 5-7/8 x 3-1/4	Ni-Cd/10 hrs.	•	Meter	0-10, TET	Combust ibles
ERDCO	07HCS		9 x 2-3/4 x 3	TI-CAVID Mrs.	ŕ	Meter +	0-1999 ppm.	Combustibles
General Monitors	170	.3	4.12 x 2/16 x 8	MC	1-2	Meter	13T - 1201-0	Combustibles
General Monitors	1100 E	2.5	4 x 6 x 1.88	Xi-Cd/10 hrs.	1-2	Neter	0-102: IEL .	Combustifies
YSX 4	20							
NSA NSA	21	9	$5-1/2 \times 3-3/8 \times 5-3/8$	D/10 hrs.	<5>	Meter	0-100' LEL	Combustibles
MSA	30							
MSA	Spotter		5-/34 x 2-9/16 x 1-1/2	Ni-Cd/?	\$ \$	Meter	0-5% CH2	CHT
MSA	2A	7	$3-3/8 \times 5-3/8 \times 5-1/2$	6xD/12 hrs.	\$\$	Meter	0-100% LEL	Combustibles
Unico	Guardian	3-1/8	$5-3/4 \times 2-1/4 \times 4-1/4$	Ni-Cd/8 hrs.		Alarm	1/3 LEL	Combustibles
Scott Aviation	D-1	7	$5-3/4 \times 3-1/2 \times 6$	D/8 hrs.		Meter	0-100° LEL	Combustibles
Scott Aviation	D-6	7	$5-3/4 \times 3-1/2 \times 6$	D/ 8 hrs.		Meter	0-107, 0-100% LEL	Combustibles
Welsh	G-70-0065	1.1	$4 \times 3-1/2 \times 5-1/2$	Ni-Cd/?	<10	Meter	0-100% LEL	Combustibles
Bio Marine	106	2-7/8	4 x 8-1/4 x 3	Ni-Cd/?	5	Meter + Alarm	0-100% LEL 0-5' CH4	Combustibles
Bio Marine	911	(19 oz.)	$3-1/4 \times 5-3/4 \times 2$	Ni-Cd/?	S	Meter + Alarm	0-100% LEL 0-5% CH4	Combustibles
Crowcon	74GC	5	2-7/8 x 5-3/8 x 5-1/2	D/?	5	Meter	0-100% LEL	Combustibles
G.F.G. (Nat'1. Mine Service Co.)	G-70 Methanometer	2	$3-3/8 \times 4 \times 1-3/4$	dry cells/300 10 sec measurements	ents	Meter	0-27, 1.8-57, CH4, 5-100Z	7н2
G.F.G. (Nat'1. Mine Service Co.)	Gasotrans	2	3-3/8 × 5 × 1-3/4	dry cells		Meter	0-50°, 9-1007 LEI.	Combustibles

NAME	CAS/VAPORS DETECTED	H2S, NH, CO or Combustibles		Various toxic gases	H ₂ S or Combustibles		Hg	Нв	Нg		Various organic compounds		H ₂ S CO		Various toxic gases and vapors	Various toxic gases and vapors	Various toxic gases and vapors	Various toxic gases and vapors
NAME	SENSITIVITY	20-500 ppm or 2 LEL	5	1-50 Ppm CL2 2-400 ppm NH3 1-1000 ppm hydrocarbons 1-100 ppm H ₂ S	either 1-500 ppm H ₂ S or % LEL		0.01 mg/m3	0.01 mg/m ³	0.02 mg/m ³		1 ppm		1 ppm 5 ppm		1-1000 ppm, depending on analytic	1-1000 ppm, depending on analytic	1-1000 ppm, depending on analytic	I-1000 ppm, depending on analytic
NUTACTURER	SICNAL	Alarm/ Meter		Meter + Alarm			Meter	Meter	Meter		Meter		Alarm/Mete Alarm/Mete		Visual	Visual	Visual	Instru- mental
NUP ACTURER NOBEL NETICHT, 1b. DIMPRS 10MS, in.	RESPONSE TIME, Sec.	09		09>	09>		3	<3	2		15		20		09 >	09 >	09 >	09>
NRY 2: SOLID STATE "MOGS" (oxidizing) GCS8 CGS8 27 oz. GCS8 S1 oz. RY 3: SOLID STATE ELECTROLYTIC RAT 10 SOLID STATE ELECTROLYTIC S1 oz. RY 4: OPTICAL (ultraviolet) S2 oz. S1 oz. RY 5: OPTICAL (ultraviolet) S2 oz.	POWER/OPER. TIME	Ni-Cd/8-12 hr		Ni-Cd/10 hrs.	Ni-Cd/10 hrs.		AC (25w)	AC (15w)	Ni-Cd/4 hrs.		Ni-Cd/?		Ni-Cd/8 hrs. Ni-Cd/8 hrs.		Ni-Cd/?	Manual	Manual	Ni-Cd/8 hrs.
NATE ACTURER HODEL WELGHT, OCS8 27 oz. CGS8 27 oz. NATIONAL STATE ELECTROLYTIC NATIONAL Sensor AG5000 5 NATIONAL Sensor AG6000 5 NATIONAL SECRETARY OF 7 NATIONAL SECRETARY O	DIMENSIONS, in.	4-3/4 × 3-3/4 × 2-1/4		4-1/8 × 5-1/4 × 7-3/4	4-1/8 × 5-1/4 × 7-3/4		4 x 5 x 17	4.5 x 8.5 x 13	4.38 x 4.75 x 11.38		5.9 x 7.4 x 18.5		8-5/8 x 4-5/8 x 4-7/8 8-5/8 x 4-5/8 x 4-7/8		× 4		× 2 ×	×
NRY 2: NRY 3: NRY 4: Ine Scienational slogy NRY 4: Ine Scienarional sach NRY 5: Tach NRY 5: Tach NRY 5: Tach NRY 6: Trine		27 02.		v	\$		8	7	9		18		3.3		77	7	1	7
NRY 2: NRY 3: NRY 4: Ine Scienational slogy NRY 4: Ine Scienarional sach NRY 5: Tach NRY 5: Tach NRY 5: Tach NRY 6: Trine	NODEL	ATE "MOGS" (exidizing) GGS8	ATE ELECTROLYTIC	AG5000	AG6000	(ultraviolet)	38D	K-23B	NV-2	(infrared)	Miran Model 101	HEMICAL	701 500 & 501	TRIC		Universal Test		МСМ
CAT CAT CAT Nat	MANUFACTURER	CATEGORY 2: SOLID STA	CATEGORY 3: SOLID STA	International Sensor Technology	International Sensor Technology	CATEGORY 4: OPTICAL	Sunshine Scientific Instruments	Beckman	Bacharach		Foxboro/Wilkes	CATEGORY 6: ELECTROCH	Bio Marine Bio Marine	CATEGORY 7: COLORIMET	National Drager, Inc.	MSA	National Environmental Instruments, Inc.	MDA Scientific, Inc.

160	Various organic gases & vapors	is and marked dis	
DETECTED	Various gases &	Halogens and halogenated compounds	A LITER ASSESSMENT OF STREET OF STREET
	6	E	
SENSITIVITY	0.1-2000 ppm	1-10,000 ppm	
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SEN	0.1	1	Februar (2. Spitz of the assumption of a service of a service of the service of t
SICNAL	-	Meter & Alarm	
SIC	Meter	Meter	
Sec			
RESPONSE TIME, sec.	ç	_	
¥ =:			
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POWER/OF TIME	Ni-Cd/10 hrs.	y y	THE COLDENS OF THE SECOND TO SELECT THE SECOND TO SELECT
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=	7	× ×	
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DIMENSIONS, 1b.	11-1/4 x 9 x 5-1/8	-3/6-	
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Z	CATECORY 8: PHOTOIONIZATION HNU Systems, Inc. PI 10	CATECORY 9: CHEMICAL IONIZATION General Electric Corp. Ferret	
	3 =	3 3	45

b. Electrochemical Cells

i. Theory of Operation

Detection of oxygen is achieved via electrochemical reaction within a small portable cell often placed at the end of a long cable for remote reading. Of the cells available, there are two basic designs in use; 1) a sealed replaceable cell and, 2) a rechargeable cell.

An example of the sealed, replaceable detector is the BioMarine Industries oxygen sensor. The BioMarine oxygen sensor is a complete sealed unit, the oxygen being allowed to diffuse through a Teflon membrane and into the electrochemical cell. Inside there are two electrodes, one gold and one lead, as well as an electrolyte solution (KOH). The current that is produced is passed through a temperature compensating thermistor and the resulting voltage is used as the signal.

Beckman Instruments, Inc., manufactures the Model 715 Process Oxygen Monitor. This oxygen monitor detects oxygen using a rechargeable electrochemical cell. "Rechargeable" refers to the ability to replace the electrolyte solution with the cell rather than replace the entire cell. The cell contains a silver anode and gold cathode which is separated from the sample by a Teflon membrane which also serves to contain a KCl electrolyte solution. As with the BioMarine sensor, oxygen diffuses through the Teflon membrane and takes part in an electrochemical reaction. In the case of the Beckman cell, the following reaction occurs:

Cathode:
$$0_2 + 2H_2O + 4e^- + 4OH^-$$

Anodes: $4Ag + 4C1^- + AgC1 + 4e^-$

When a DC voltage is applied to the electrodes, oxygen is reduced at the cathode, causing a current to flow. The magnitude of the current is proportional to the amount of oxygen present in the sample.

ii. Specifications of Selected 02 Monitors

• BioMarine Industries, Model OA22R, Oxygen Deficiency Detector

Range: 0-40% 02

Dimensions: $2 \times 2-1/2 \times 5$ in.

Net weight: 14.5 oz.

Response time: 90% in less than 10 sec.

Linearity: ±1% full scale at constant temperature

Accuracy: ±1% 02

Temperature compensation error: Maximum ±5% in 32-104°F (0-40°C)

Power Supply: None required

• MSA Co., Models 244, 244R, Oxygen Indicators

Range: 0-25% 02

Dimensions: 2 x 2-1/2 x 5 in. (Amplifier-Meter case)

1-11/16 dia. x 1-1/2 in. depth (remote sensor)

Net weight: 11 oz. (hand-held Model 244)

15 oz. (remote sensing, Model 244R)

Response Time: 90% in less than 20 sec.

Linearity: ±1% of full scale at constant temperature Accuracy: ±1% of full scale at constant temperature

Temperature compensation error: Maximum ±5% of full scale in the range

32-104°F (0-40°C) when calibrated at 68°F (20°C)

Power supply: Batteries

• Beckman Model 715, Process Oxygen Monitor

Range: 0-25% 02, 0-5% 02

Dimensions (approximate): 10 x 8 x 2 in.

Net weight: 10 lb.

Response time: 90% in 20 sec.

Linearity: ±0.75% of full scale with recording output

Accuracy: ±1% of full scale at constant temperature, ±6% in range of

32-110°F (0-44°C)

Temperature compensation error: 32-110°F (0-44°C) - ±5%

90-90°F (15-32°C) - ±2%

Power supply: One 1.34v and two 6.75v self contained mercury cells

iii. Important Operating Characteristics

• BioMarine Industries, Model 0A22

The calibration required for this type of sensor (sealed cell, replaceable) is done with normal air, no special gases are required. Cell may require frequent replacement which is done at an annual cost of \$38. For high humidity environments (rain), an adapter is provided to eliminate any interference. The unit is intrinsically safe, MESA-approved and requires no power supply.

• MSA Models 244, 244R

One point calibration is performed with uncontaminated fresh air. Model 244 is approved by the Bureau of Mines for use in mines. Replacement of cell is required with the cell having an approximate life span of 120,000 percent 0_2 hours $(6,000 \text{ hours at } 20\% \text{ } 0_2)$.

• Beckman Model 715, Process Oxygen Monitor

This 0_2 monitor can be used in humidities up to 95% and ambient temperatures of $32-122^{\circ}F$. The batteries needed have a life-span of approximately one year and the service interval for the sensor (recharging the electrolyte) is every 3-6 months. Calibration can be done with ambient air. Stability of the sensor is said to be 1% within a 24-hour period.

c. Galvanic Cell

i. Theory of Operation

The detection of oxygen is based on the principle of a primary galvanic cell. The cell consists of a positive carbon electrode and a negative zinc electrode. The electrodes are immersed in an electrolyte solution. When no oxygen is present, the carbon electrode is polarized, inhibiting the flow of current. When oxygen is present, it diffuses through the carbon electrode and depolarizes it. This allows current to flow in proportion to the oxygen concentration.

ii. Specifications, MSA Portable Oxygen Indicators, Models E & S

Range: 0-25% 02 (Model E), 5-40% 02 (Model S)

Dimensions: $6-3/4 \times 4-1/8 \times 5-3/4$ in.

Weight: 5-3/4 1b.

Accuracy: ±5% of full scale (Model S) ±2% of full scale (Model E)

d. Solid State Electrochemical

The only commercially available solid state oxygen monitor uses doped zirconium dioxide (ZrO₂) as the sensing element. Present day devices are not portable; however, the state-of-the-art has reached the point where miniaturization can be readily achieved if necessary.

The ZrO₂ gauge consist of a solid electrolyte, calcia-oryttria-doped ZrO₂, with porous inert electrodes on two sides. When the electrodes are exposed to atmospheres containing oxygen at different partial pressures, an emf is generated according to the Nernst equation

$$E = \frac{RT}{4F} \ln \frac{P(1)}{P(2)}$$
 (1)

where R is the gas constant, F the Faraday and T the absolute temperature. If oxygen pressure P(1), for example, is held constant, then the emf generated is a measure of the unknown oxygen pressure P(2).

The ZrO₂ gauge is specific for oxygen and has fast response. A wide range of concentrations can be handled but to date most units are used for combustion, exhaust gas control or furnace atmosphere control. Advantages are speed, specificity and elimination of sampling requirements. The major disadvantage of the ZrO₂ oxygen gauge is that to obtain significant oxygen ion transport, and hence ionic conductivity, the cell must be operated at temperatures in the range of 600°C to 700°C. While this does not present a problem with respect to miniaturization, it does require a relatively large amount of power. The power requirements can be reduced by using thin film cells where stable operation can be observed

at temperatures at low as 300°C. Thus, for example, a cell consisting of thin films of a Ni-NiO mixture, calcium-stablized zirconium and porous platinum as been prepared (Greene 76) which yielded stable emf data at 283°C. The Ni-NiO mixture acted as a reversible reference electrode. Other buffers that have been used (Kleitz 74) include Pd-PdO and Cu-Cu₂O. Table 3 lists the manufacturers of ZrO₂ gauges and some characteristics of commercial devices.

3. Flammable Vapor Monitors

a. Introduction

Two basic types of flammable vapor detectors are avilable from commercial vendors. One is based on catalytic oxidation of combustible substances, principally organic vapors, by a heated element. The oxidation reaction produces a small temperature change in the catalyst support in an integral temperature-sensitive device, which charge is converted into an electrical signal that activates the meter or alarm. These monitors are widely used for their intended purpose, which is to measure concentrations of oxidizable organic vapors in the range of about 100 ppm to 10,000 ppm (0.01-1%) in air. They are non-specific (except for oxidizable substances as such) and are therefore well-suited to the task of detecting any combustible substance in the usual flammable range of 0.5-5%.

The other type is the metal oxide gas sensor (MOGS), a more recent innovation which operates on a somewhat different principle and has a somewhat greater sensitivity, extending to a few ppm of oxidizable vapors in air. Although it is used as a combustible vapor detector in some devices, its electrical output signal tends to become saturated at the high concentrations associated with flammability. It is therefore generally preferred for detection of lower concentrations typically associated with human toxicity limits.

b. Catalytic Detectors (Category 1, Table 3)

The principle on which catalytic detectors operate is the measurement of heat liberated when an organic molecule reacts exothermically with an oxidant. In a gaseous atmosphere containing oxygen, together with small amounts of oxidizable organic vapors or gases, this reaction can be made to occur selectively at the surface of a suitable solid catalyst. This catalyst, which must ordinarily be maintained at some elevated temperature (usually above 300°C), must then be associated with a sensitive temperature-sensing element which can measure the small amount of additional heat produced by the catalyzed reaction. In effect,

the sensor unit must be a miniature calorimeter, capable of measuring temperature changes resulting from the evolution of heat at levels as low as 100 kilocalories per mole.

In order for the sensor to operate continuously as a detector of oxidizable vapors, both the organic molecules and atmospheric oxygen molecules must be able to be adsorbed momentarily on the catalytic surface. The reaction products must not be strongly sorbed, however, since they must be discharged in order to make room for the arrival of new reactants. The temperature of the catalyst is controlled at a point high enough to assure that the rate of the reaction exceeds that of the diffusion of molecules in the gas phase to and away from the surface. The amount of heat produced is then directly proportional to the amount of oxidizable components in the gaseous atmosphere around the detector.

In modern devices of this kind, two kinds of catalytic substances have been shown to be effective. They are the so-called "platinum metals," platinum, rhodium, palladium and iridium; and a class of transition metal oxides, the best known of which are the Hopcalites, complex mixed oxides of coppoer and manganese. The platinum metals are generally formed into fine filaments which can be heated by their own resistance to an electric current, and whose temperature changes, due to the occurrence of oxidation reactions on their surface, can be detected as changes in resistivity. The Hopcalite type of catalyst, which is inherently a poor thermal conductor, must be used as a coating on a heated thermistor, a requirement that imposes some practical difficulties on its operation and limitations on its sensitivity. Table 3 lists the principal manufacturers of catalytic devices and the important characteristics of these devices.

b. Metal Oxide Sensors (Category 2, Table 3)

The semiconducting metal oxide gas sensor (MOCS) will detect flammable vapors. The sensitivity of the detectors is such, however, that at levels well below those usually associated with flammability, typically a few hundred ppm, the sensor becomes saturated and hence would have limited utility for warning at the appropriate concentrations. For this reason, these sensors are better suited to the detection of oxidizable vapors at concentrations more closely related to toxic limits. Their characteristics will therefore be discussed in Section B.4, Toxic Vapor Detectors.

4. Toxic Gas and Vapor Detectors

a. Introduction

A considerable variety of detectors are offered commercially for the purpose of monitoring the air for various toxic gases and vapors. Some of the most important examples are listed in Table 3. Because most toxic vapors are organic chemicals (note the distribution of "Category 23: Inorganic" vs. "Categories 1-22: Organic" in Column III of Table 1), the available detectors are largely designed to detect that kind of substance. In fact, the most widely applicable of the currently available personnel-

monitoring devices are based on the metal oxide gas sensor (MOGS) or the more recent "electrolytic semiconductor" sensor offered by International Sensor Technology. Other types of sensors are based on optical absorption, photoionization, color-forming chemical reactions, flame ionization and chemical ionization. Adaptations of mass spectrometry, gas chromatography and infrared spectrophotometry offer the advantage of greater compound-specificity than many other devices (with the notable exception of chemical color-forming sensors), but generally require more complex and massive hardware than is suitable for personnel monitoring requirements.

b. Semiconducting Metal Oxide Detectors (Category 2, Table 3)

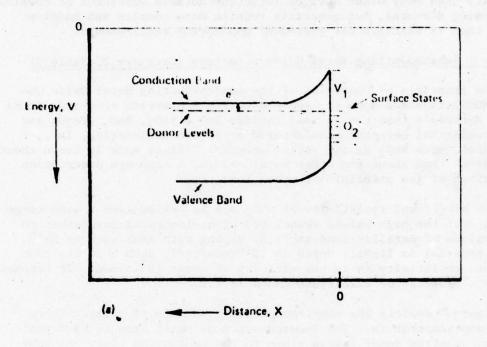
The principle of operation of the semiconducting Metal Oxide Gas Sensor (MOGS) is based upon the semiconductive properties of n-type metal oxides. Materials that can be used include SnO2, TiO2, ZnO, Fe2O3 and WO3. A commercial detector manufactured by Figaro Engineering, Inc., Osaka, Japan, uses SnO2 as the active material. Since more is known about this material than about the other metal oxides, a complete description will be given of its principle of operation.

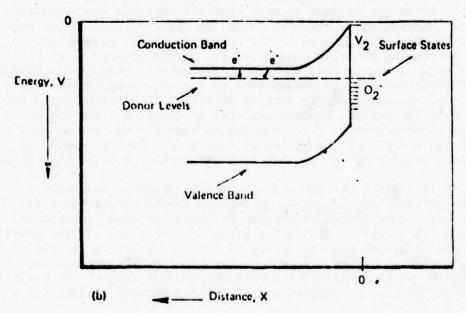
The electrical resistivity of SnO₂ can be varied over a wide range extending from the high values associated with electrical insulators to the low values of metallic conductors by doping with ions such as Sb^{+5} . When the material is lightly doped ($\sim 10^{16}\mathrm{ions/cm^3}$), such that its room temperature resistivity is in the vicinity of about 10^3 ohm-cm, it becomes useful as a detector of oxidizable gases in air.

Figure 2a depicts the electronic band structure of lightly doped SnO_2 at room temperature. The incorporation of small amounts of dopant introduces electron donor levels close to the conduction band. As long as the donor levels are located no more than 0.1 eV below the conduction band at room temperature, a fraction (~10%) of the electrons in the donor levels will be thermally excited to the conduction band, thereby substantially increasing the bulk conductivity. In the absence of an electric field or of optical excitation, and in the presence of atmospheric oxygen, the donated electrons will be compensated by the chemisorption of oxygen on the surface. Adsorbed oxygen acts as an efficient electron trap, so the region near the surface becomes depleted of electrons, causing the energy bands to bend upward, i.e., the region near the surface becomes more positive on the energy scale depicted in Figure 2a. The net result is that an energy barrier is set up that inhibits further flow of electrons.

Figure 2b depicts the situation at higher temperatures, when a large number of electrons are thermally excited to the conduction band. When this occurs, more oxygen is chemisorbed until at some temperature, T_{max} , all available surface adsorption sites are occupied. If the temperature is increased beyond that necessary to achieve saturation of the surface with adsorbed oxygen, the concentration of bulk electrons increases, but since there can be no additional chemisorption of oxygen, the resistivity decreases. The effect of temperature upon the electrical resistivity of

Figure 2
SnO₂ Band Structure at a) Room Temperature (\sim 25°C)
and b) High Temperature (200°C). In the Figure, V₂ > V₁





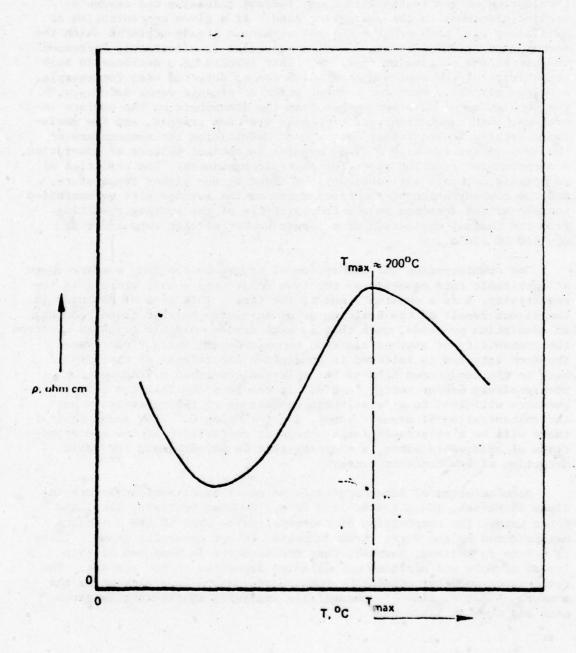
SnO2 is shown schematically in Figure 3. In normal operation, the temperature of the surface is held constant, ideally, for most purposes, in the vicinity of T_{max} .

When oxidizable organic molecules approach the SnO2 surface, the chemisorbed oxygen reacts with them, thereby releasing the oxygen's trapped electrons to the conduction band. At a given concentration of oxidizable gas, this process quickly attains a steady-state in which the normal population of adsorbed oxygen molecules is effectively decreased because of the continuing reaction. This results in a decrease in bulk resistivity of the semiconductor which can be detected via, for example, a bridge circuit. When the concentration of organic vapor decreases, the population of adsorbed oxygen from the atmosphere on the surface increases, more conduction band electrons are thus trapped, and the resistance returns to its former low value. Maintaining the temperature of the SnO2 in the vicinity of Tmax assures an optimal balance of adsorption, desorption and reaction rates for most circumstances. The oxidation of an organic molecule will obviously be aided by the higher temperature, and the concentration of reactive oxygen on the surface will be maximized because of the increase in electropositivity of the surface resulting from the thermal excitation of a larger number of electrons under an applied DC field.

The chemisorption and desorption of oxygen on the SnO2 surface obeys a logarithmic rate equation of the type $d\rho/dt\,^{\sim}$ exp (-bp), where ρ is the resistivity, b is a constant, and t, the time. This type of behavior is the direct result of the building up of an energy barrier (band bending) as adsorption proceeds, such that as each oxygen molecule traps an electron the probability of another electron surmounting the barrier decreases. The same rate law is followed in desorption and release of electrons back to the conduction band as the released electrons originate from progressively deeper energy levels. It can be shown that the time dependence will lead to a logarithmic dependence of the resistivity upon the concentration of organic vapor, i.e., $\rho \sim \text{Log C}$. This means that there will be a relatively large change in resistivity at low concentrations of oxidizable vapor, a property that is advantageous for rapid detection of low concentrations.

Manufacturers of detectors based on metal oxide semiconductors include Bacharach, Inc.; the Bullard Corp.; General Monitors, Inc.; and EnMet Corp. The composition of the metal oxide used in the detectors manufactured by the first three companies is not generally known. There is reason to believe, however, that the detector is composed of thin layers of MoO₃ and platinum or palladium deposited on the surface. The toxic vapor detector offered by EnMet Corp. uses a SnO₂ element as the sensor. A description of commercially available instruments is given here and also in Table 3.

Figure 3
Resistivity of SnO₂:Sb



i. EnMet Gas Detectors

Task I Criteria

Weight (CGS-8&10): Dimensions (CGS-8&10): Sensitivity (CGS-8):

Sensitivity (CGS-10):

Power Requirements:
Operating Time (CGS-8):
Operating Time (CGS-10):
Price (CGS-8):
Price (CGS-10):
Response Time (CGS-8&10):
Signal (CGS-8&10):

Product Data

27 oz.

4-3/4 x 3-3/4 x 2-1/4 in.

20 ppm (combustible gases)

50 ppm CO

20 ppm (combustible gases)

50 ppm CO,

10-6 - 1 atm O2

Ni-Cd batteries

12 hours

8 hours

\$325 - \$405

\$445 - \$505

60 seconds (90%)

Alarm, visual (LED)

& audio; meter optional

ii. Bacharach Sentox H₂S Detector

Task I Criteria

Weight:
Dimensions:
Sensitivity:
Power Requirements:
Operating Time:
Price:
Response Time:

Response Ti Signal:

Product Data

7 1bs.
10.5 x 6.75 x 6.5 in.
0-50 ppm H₂S
Ni-Cd
8 hours
\$1,045
108 seconds (90%)
Meter

iii. Bullard H₂S Detectors (2104 H; 2104 HB)

Task I Criteria

Weight (H & HB):
Dimensions (H & HB):
Sensitivity (H & HB):
Power Requirements (H & HB):
Operating Time (H & HB):
Price (H & HB):
Response Time (H):
Response Time (HB):
Signal:

Product Data

5.5 lbs. 4.1 x 5.3 x 7.4 in. 0-50 ppm H₂S Ni-Cd 8 hours \$895 98 seconds (90%) 151 seconds (90%) Meter

iv. General Monitors H2S Detectors

Task I Criteria

Weight: Dimensions: Sensitivity:

Power Requirements: Operating Time:

Price:

Response Time:

Signal:

Product Data

4 1bs. 4.25 x 4.15 x 9.85 in. 0-50 ppm H₂S AC

\$1,409 17 seconds (90%) Meter

c. Solid State Electrolytic Cell Gas Sensor (Category 3, Table 3)

A recent development in the field of air quality monitoring technology is a device identified by its developers as the Solid State Electrolytic Cell Gas Sensor. Except for the manufacturer's own literature, little or nothing of a written nature is available to describe this technology, but it appears to be similar in many respects to that of the metal oxide gas sensors. The developer claims some notable differences for his system, however, such as the fact that it can detect gases without the presence of oxygen, and the fact that it is capable of detecting reducible gases such as chlorine, as well as oxidizable substances such as hydrocarbons, ammonia, carbon monoxide, hydrogen sulfide and hydrogen.

Advertised minimal detectable concentrations extend to 1 ppm in air for hydrogen, chlorine, and hydrogen sulfide, and extend to the low ppm range for various hydrocarbons, ammonia and carbon monoxide. Maximum detectable concentrations are about 1000 ppm for the latter group of vapors, and a few hundred ppm for the former.

The manufacturer's Model AG 5000 is a universally applicable portable instrument that accepts different types of sensor elements (for detecting different substances), weighs five pounds and operates for ten hours on rechargeable Ni-Cd batteries. The Model AG 600 has a switch-selectable capability of detecting either $\rm H_2S$ or % LEL for hydrocarbons. In either setting, the detector is said to be free of interference from the other substance, even though the levels of concern are quite different (1-200 ppm for $\rm H_2S$ vs. 100-10,000 ppm for hydrocarbons). In addition to the substances cited, the manufacturer claims that the device is effective for monitoring sub-toxic levels of carbon disulfide, Freon-22, hydrogen cyanide, methyl bromide, methyl chloride, tetrachloroethylene and vinyl chloride.

d. Optical Detectors: Ultraviolet Absorption (Category 4, Table 3)

Ultraviolet absorption photometers have been available as commercial items for the detection of mercury vapor and, in some instances, for benzene and other ultraviolet-absorbing organic vapors. Because the 254 nm radiation sources in these detectors are mercury lamps, their use for detection of mercury vapor is an ideal application. Their sensitivity is very high, and their specificity is very good, if considered on an atom-for-atom basis. The presence of relatively large concentrations of benzenoid aromatic compounds in the air is also detectable, but this is not the preferred method for monitoring of those compounds.

Only one manufacturer was found to be offering a battery-operated unit that fits U.S. Coast Guard specifications for personnel monitoring, but presumably other manufacturers would be capable of adapting their products to meet similar requirements. The following descriptive information was obtained from manufacturers of three mercury vapor detectors.

Model No.	Beckman Model K-23-B	Sunshine Model 38D	Bacharach Model MV-2
Dimensions (Inches)	4.5 x 8.5 x 13.0	4 x 5 x 17	4.38 x 4.75 x 11.38
Weight (lbs.)	7	8	6
Power	115V; 50/60 Hz; 15W	110V; 60 Hz; 25W	12V; NiCd battery (rechargeable; 4-hr operation, time/charge)
Sensitivity (mg/m ³)	< 0.01	0.01	< 0.02
Response Time	"Instantaneous"	2-3 sec	90% by 5 sec ∿ 5 min warm-up required
Cost	\$1350	\$1245	\$1180

The indication of the presence of mercury is shown on a direct reading dial.

e. Optical Detectors: Infrared Absorption (Category 5, Table 3)

A relatively high degree of selectivity is attainable for the detection of vapors of organic compounds in air by the use of infrared absorption spectrometry. Portable spectrometers are offered by at least one commercial manufacturer (Foxboro/Wilks, Inc.) which have adequate sensitivity for the detection of almost all toxic organic vapors at levels of concern to the Coast Guard. While the smallest of these devices is somewhat larger and heavier than present requirements would allow, the principle is an attractive one and the feasibility of reducing the size and weight to meet U.S. Coast Guard needs is probably reasonably high.

Data on three models of Foxboro/Wilkes Miran analyzers are presented here for illustration:

Model Selectivity	Model 101	Model 103	Model 104
hours to	Fixed filter for specific compound	Interchangeable Filter/Meter Sets	Adjustable filter & Path Length
Dimensions (Inches)	5.9 x 7.5 x 18.5	7.5 x 11.0 x 22.4	6.7 x 9.8 x 22.4
Weight (lbs.)	18	23	24
Power Requirement	a) 115/220V or b) 7.2V, 1 amp NiCd rechargeable battery	115/220V, 25W	
Sensitivity (ppm)	The state of the simultane will be wellen.	readout only; the	To see a see a see see see see see see see
Response Time (Sec)	15 sec	15 sec osla el il	Selectable 1, 4, 10 and 40
Cost	a) \$2630 b) \$2950	\$3680 + \$240/set of filters	\$5450

e. Electrochemical Monitors (Category 6, Table 3)

(i) Model 701 Hydrogen Sulfide Monitor (Bio Marine Model 701)

Hydrogen sulfide is drawn into the monitor by means of a built-in diaphragm pump which employs a brushless DC motor. The molecules diffuse through a Teflon barrier to an electrochemical cell having Pt and PbO electrodes in sulfuric acid electrolyte. Molecules are oxidized at a sensing electrode and an electrical current is generated which is proportional to the concentration of hydrogen sulfide. This current is electronically sensed by the proprietary sensor and is displayed as ppm of $\rm H_2S$ on the front panel meter.

Meter scales are calibrated in 0-20 and 0-100 ppm $\rm H_2S$. Selection of the scale range is made using a slide switch located below the meter. A unit test switch is provided which allows testing of all alarm functions and battery conditions.

The Model 701 is automatically temperature compensated over the range 0° to 40°C. Performance is accurate in 95% R.H. environments. The audio/visual alarm system is activated when the $\rm H_2S$ concentration exceed the user-adjusted level. Alarms are also activated if the battery charge is low or if the sample flow is interrupted.

The 701 has the capability of providing periodic sampling, during which the unit is active for 20 seconds every three minutes. When the unit is used in this manner, the battery life extends from eight hours to 70 hours.

An "Interfering Cases Filter" composed of potassium permanganate is used to eliminate interferences due to CO, SO_2 and NO. Without the filter, approximately equivalent response is obtained for 10 ppm H₂S or 50 ppm CO.

(ii) Models 500 and 501 Carbon Monoxide Gas Detectors

The model 500 and Model 501 Carbon Monoxide Gas Detectors use the same detector components and operating principles as the Model 701 Hydrogen Sulfide Monitor. Meter scales calibrated in 0-100 and 0-500 ppm CO ranges are substituted for the $\rm H_2S$ monitor's unit. The Model 500 possesses a meter readout only; the Model 501 has simultaneous audio/visual alarms for preset gas concentration, low pump flow, and low battery charge. It is also capable of periods of continuous sampling.

Specifications for both types of detectors are given below.

Model 701 H₂S Monitor

Size: 8-5/8"H x 4-5/8"W x 4-7/8"D

Weight: 3 lbs., 6 oz.

Response Time: 20 seconds

Ranges: 0-100 ppm, 0-500 ppm

Temperature Operating Range: 0°C-40°C

Accuracy at Constant Temperature: + 5%

Humidity Range: 15% to 100%

Battery Life: Operating continuously = 8 hours

Periodic sampling = 70 hours Recharge time = 16 hours

Cell Life: 1 year, minimum

Models 500 & 501 CO Gas Detectors

Size: 8-5/8"H x 4-5/8"W x 4-7/8"D

Weight: 3 lbs., 6 oz.

Response Time: 20 seconds

Ranges: 0-20 ppm, 0-100 ppm

Temperature Operating Range: 0°C-40°C

Accuracy at Constant Temperature: + 5%

Humidity Range: 15% to 100%

Battery Life: Operating continuously = 8 hours

Periodic sampling = 70 hours Recharge time = 16 hours

Cell Life: 1 year, minimum

f. Colorimetric Monitors (Category 7, Table 3)

One of the oldest and most widely used types of monitors for chemical air pollution is the one based on color-forming chemical reactions. Several well-known commercial brands of these devices are the length-ofstain tubes offered by National Draeger, Inc., Mines Safety Appliances, National Environmental Instruments, Inc., and MDA Scientific, Inc. Although a number of different systems have been developed, some involving crayons and some with impregnated paper tapes, the most popular have been those that use an inert granular support on which a color-forming reagent is deposited. The coated granules are packed into a short section of transparent glass tubing which is sealed at both ends until it is to be used. In use, the tube ends are opened and the air to be analyzed is pumped through the tube at a known rate. Specific contaminants in the air react with the color-former, such that a constantly lengthening stain of visible color progresses along the length of the tube. Because these tubes are cumulative detectors, special methods have to be applied to permit them to read momentary concentrations.

One manufacturer, National Draeger, Inc. offers an automatic readout device called a "Polymeter" which uses the chemical color-forming reactions as the basis for sensing a variety of contaminants and which displays the results as an electrical meter or visual alarm.

Another manufacturer, MDA Scientific, has developed impregnated papertape monitors that can give real-time indications of dangerous concentrations of two gases, toluene diisocyanate and phosgene, and are expected to be able to detect other gases in the near future. Presently available models that are small enough to be suitable for personnel monitoring, weighing about two pounds and operating on rechargeable NiCd batteries, do not give a real-time alarm, but rather produce a cumulative record of exposure dose. The manufacturer states that a real-time alarm version will be available within a year.

g. Photoionization Detector (Category 8, Table 3)

(i) Theory of Operation

The basic principle of operation for this detector is photoionization. A variety of different compounds can be measured by this technique including many organic, some inorganic and even organometallic compounds.

The heart of the photoionization detector is an ultraviolet (UV) lamp. Photons (10.2 eV in energy) are emitted from the lamp and pass through a transmitting window (MgF $_2$) and enter into an ionization chamber where contact with the organic vapor is made. Absorption of the UV radiation by molecules possessing an ionization potential of less than 10.2 eV leads to ion formation:

$$RH + hv \rightarrow RH^{+} + e^{-}$$

Electrons are captured by a collector after acceleration by a high voltage electrode. With a UV-absorbing matrix gas such as nitrogen or air, the following reactions can also occur to produce ions:

$$N_2^* + hv \rightarrow N_2$$

$$N_2^* + R + N_2 + R^+ + e^-$$

The net effect of the above reactions is that molecules with ionization potentials up to 10.5 eV may be measured by the photoionization detector.

(ii) Specifications for the Model PI 101 (HNU Systems, Inc.)

Substances detected: most organic vapors (see Table 4 for relative sensitivities)

Range: 0.1 to 2000 ppm

Detection limit: ~ 0.1 ppm

Linear range: 0.1 to 600 ppm (can vary with compound)

Useful range: 0.1 to 2000 ppm

Response time: < 5 sec to 90% full scale

Ambient humidity: to 95% R.H.

Physical dimensions and weight:

Probe: 2.4 inches x 11.2 inches (length); 20 oz.

Readout, power supply: 8-1/4 inches (width) x 5-1/8 inches

(depth) x 6-1/2 inches (height);

7 pounds

Stowed: 8-1/4 inches (width) x 5-1/8 inches (depth) x

9-1/2 inches (height); 12 pounds

Power Requirements: Operating Time

Continuous use, NiCd battery: > 10 hours

Recharge time, max: < 14 hours, 3 hours to 90% full charge

Recharge current, max: 0.4 Amps @ 115 Vac

(iii) Operating Characteristics

The operation of the Model PI 101 photoionization analyzer is characterized by stable baseline, low noise and reproducible response. Response to major components of air such as O_2 , N_2 , CO, CO_2 and H_2O is essentially zero. Sensitivity to various organic compounds is given in Table 4:

 $\frac{{\tt Table}\ 4}{{\tt Relative\ Photoionization\ Sensitivities\ for\ Various\ Gases}}$

Chemical Grouping	Relative Sensitivity	Examples
Aromatic	10.0	Benzene, Toluene, Styrene
Aliphatic Amine	10.0	Diethylamine
Chlorinated Unsaturated	5-9	Vinyl Chloride, Vinylidene Chloride, Trichloroethylene
Carbony1	5-7	MIK, MIBK, Acetone, Cyclohexanone
Unsaturated	3–5	Acrolein, Propylene, Cyclohexene, Allyl Alcohol
Sulfide	3-5	Hydrogen Sulfide, Methyl Mercaptan
Paraffin (C ₅ - C ₇)	1-3	Pentane, Hexane, Heptane
Ammon 1a	0.3	
Paraffin (C ₁ - C ₄)	0	Methane, Ethane

Comparison to flame ionization detection is useful since that detector's response characteristics are fairly well known. This is given in Table 5.

Calibration of the detector is fairly simple and can be done in the field, using analyzed gas mixtures and a gas sampling bag. Required frequency of calibration, however, is quite low in comparison to conventional detection systems. At maximum gain (0-2 ppm full scale), a span drift of less than 0.02 ppm over 14 days can be expected.

Additional characteristics of the detector are: no need for portable gas supplies; only two moving parts (pump and meter); inert materials; and electronic zeroing.

h. Chemical Ionization Detectors (Category 9, Table 3)

A proprietary type of detector, used as the sensing element in several models of halogen leak detectors and a toxic vapor monitor offered by General Electric Instrument Products Operation, functions on an unusual principle involving chemical reation of halogens and halogencontaining compounds with an alkali element that is emitted from a heated ceramic substrate. The alkali-halide vapor thus produced is ionized on a heated platinum wire as a result of an impressed DC potential between the ceramic emitter and the platinum collector. Current flow through the vapor phase is proportional to the concentration of halogen (or halogenated substance) in the air. Amplification of the current allows a visual or audible slarm to be tripped.

General Electric offers several different types of monitors based on this principle. The TVM-1 Toxic Vapor Monitor is the most versatile of the group. The manufacturer cites seventy-five (75) different halogen-containing substances as being detectable at concentrations ranging from fractions of ppm to over 1000 ppm. Chlorine and chlorinated compounds are detected with greatest sensitivity, and fluorine and its compounds are detected with about 100-fold less sensitivity. Both organic and inorganic halogen compounds are detectable. The TVM-1 is too large for use as a personnel monitor, measuring 11-3/4" x 6-1/2" x 12-3/4" and weighing 23 pounds. It is powered by 117 or 234 VAC at either 50 or 60 Hz. Its readout is by meter and both video and audio alarm.

The Ferret is a high-sensitivity version of the TVM-1, adapted specifically for detection of leaks of dichlorodifluoro-methane (R12) and similar refrigerant gases. The unit is slightly smaller and lighter than the TVM-1, and has fewer adjustable settings. Its meter is calibrated in "leak rate" rather than in "ppm," but in all essential aspects it closely resembles the TVM-1.

Table 5

Comparison of the Relative Sensitivities of the Photoionization and Flame Ionization Detectors

Compound	PID Response	FID Response	Ratio PID/FID
Toluene	4.10	0.18	34
Benzene	6.00*	0.16	38
1,3 Butadiene	5.20	to have the set	
Diethyl Sulfide	5.20		
p-Xylene	5.03	0.15	34
Carbon disulfide	4.20	0	
Propylene	3.90	emine : This term	
Methyl ethyl ketone	3.72	60 in <u>2</u> 6 com	
Allyl alcohol	3.40	e resulta d e y as mos	
Dimethyl sulfide	3.25	<u>-</u>	
Acetone	3.04	0.06	51
Cyclohexene	2.44	ventilo kale	
Acrolein	2.70		
Trichloroethylene	2.76	0.08	35
Vinyl chloride	2.44	0.06	41
Tetrahydrofuran	1.86		
Pyridine	1.78		
Ethylene	1.34	0.07	19
Hexane	1.23	0.15	8.2
Cyclohexane	0.90		
Ethanol .	0.81		

^{*}All values (PID and FID) were normalized to Benzene = 6.0 on PID

The Tracker is a pocket-size battery-operated portable instrument which was designed for use by servicemen in locating leaks of R12 and similar gases from refrigeration systems. The Tracker weighs 18 oz., measures 3.2 x 7.3 x 1.8 inches, is powered by two D-size alkaline batteries, and has a response time of one second. Its readout is by preset audio and video alarms. Its sensitivity is said to be lower than those of the Ferret and the TVM-1, but may still be adequate for U.S. Coast Guard purposes. The manufacturer has not evaluated the Tracker as a toxic vapor monitor and does not advertise it for that purpose. Neverthless, since its principle of operation is said to be identical to that of the other halogen-sensitive monitors made by this company, there is every reason to expect that it could be used for that purpose.

Miniature Gas Chromatograph

A miniature gas chromatography (GC) system has recently been developed using integrated circuit technology. The system consists of the following components, all of which are placed on a 5-cm diameter silicon wafer: an open tubular capillary column, two sample injection valves, and a thermal conductivity detector. (Terry, 1975)

The capillary column is created by etching a spiral groove 3 meters in length into the surface of the silicon wafer. The column is $\sim 200~\mu m$ wide and 20 μm deep. Ordinary GC liquid phases coated on the inside walls of the capillary and provide the column with an ability to separate components of the sample injected.

The sample injection system is comprised of two pneumatically-actuated diaphragm valves constructed with silicon diaphragms and seats. The dead volume of the injection system is only 4 nanoliters. The valve system is capable of introducing reproducibly 20 nanoliters of sample vapor into the carrier gas stream.

The thermal conductivity detector used is a 125-µm diameter thermistor bead sealed in a cavity at the output end of the capillary. The detector is capable of detecting vapor concentrations of 1 ppm.

A miniature GC system has been designed and fabricated which will separate isobutane, acetone and ethanol using a 0.5-meter column and a carrier gas flow rate (helium) of 1.7 μ L/sec. A sample size of 50 nL was used. The separation was performed in 40 seconds.

j. Plasma Chromatography

The technique of plasma chromatography (PC) has received considerable attention during the past several years as a promising method for ultratrace analyses of organic substances. The plasma chromatograph can be likened to an electron-capture chromatographic detector connected to a time-of-flight mass spectrometer operating at atmospheric pressure. The sample to be analyzed is swept into an ion source in a stream of

either nitrogen or air carrier gas containing a trace of water vapor. The 60-kev beta particles emitted from a 63 Ni source first react with the carrier gas to produce both positively and negatively charged reactant ions (Karasek, 1974). The positively-charged ions include $({\rm H_2O})_{\rm nH^+}$ (${\rm H_2O})_{\rm n}$ NO+ ions; while the negatively-reactant ions have been identified as CN , C1 , NCO , $O({\rm H_2O})_{\rm Z}$, and $CO_{\rm 3}$ (Carr, 1977). The reactant ions can then undergo ion-molecule reactions with a trace level organic molecule (M) to produce positive ions such as MH+ and (M)NO+. If the trace organic substance has electron-capturing tendencies, negative reactions products can also be produced, e.g., halide ions from alkyl halides or the negatively-charged molecular ions in the case of nitrobenzene.

Other molecules when present in large quantitity, e.g., benzene solvent, can also function as a reagent gas in the ⁶³Ni source. In fact, the Hornings and co-workers at Baylor (Carroll, 1974) have developed a technique called atmospheric pressure ionizat. (API) mass spectrometry by combining a plasma chromatograph ion source with a mass spectrometer. The formation of ions in the PC source is quite analogous to that which occurs in chemical ionization mass spectrometry; the primary difference is that chemical ionization is carried out at about one torr and the PC source operates at 760 torr.

Once formed, in the PC ion source, a pulse of the ions is injected into a drift spectrometer which is exactly analogous to a time-of-flight mass analyzer except that the drift spectrometer is filled with very pure nitrogen and operates at atmospheric pressure. Thus, the time-of-flight for a particular ion is determined by collision interactions between the ion and nitrogen molecules.

C. TASK III: EVALUATIONS AND RECOMMENDATIONS

General Remarks

Our evaluation of available personnel monitoring devices and applicable technology has necessarily been limited to information published by manufacturers and by other investigators, since no actual laboratory field testing was conducted in connection with the present program. It is therefore important to realize that the statements, observations and conclusions given in the following sections are based only on apparent characteristics, and should not be taken to imply any endorsement or criticism of actual performance of any device or system.

In general, we have been guided by the criteria for characteristics and performance established in Task I. We recognize, however, that some of those criteria are not yet fixed or fully developed, and that much depends on the alternatives for protective equipment that become available during the next year or two. In addition, the question of how much information will actually be available on identity of hazardous substances in the air around the scene of a spill is yet to be answered, there being a number of still unsolved technical problems associated with making such an identification in the field. Finally, with respect to the toxicity of substances for occasional short-term exposure, although we have cited two sets of values which have been proposed for such exposure, the list is by no means complete, and some of the proposed values themselves are still susceptible to debate and to confirmation. For instance, exposure to known carcinogens may require different criteria from those applied to other chemical substances.

Our evaluation of individual monitoring capabilities is organized into four headings, covering the four types of monitoring with which the present investigation has been concerned: oxygen deficiency, flammable limits, toxic vapors and suit-damaging chemicals. It has been assumed that toxicity is limited to inhalation of vapors, inasmuch as the present protective suit and the XM-41 air filter effectively protect against other types of toxic substances. Our general observations are that of the four categories, only the last two: toxic vapor monitoring, and suit damage monitoring, require additional research and development to meet U.S. Coast Guard needs.

The data on weight dimensions, power requirements and other physical characteristics are tabulated for convenient comparison in Table 3. Suitability of the various types of detectors for detection of gases and vapors at flammable and/or toxic limits are given in Table 1 for substances on the "Chris Phase I" list whose vapor pressure at 40°C are high enough to produce concentrations in excess of those limits. Other substances of potential concern to Strike Team personnel but for which comparable data are not available are listed in Table C-2 of Appendix 2. Column XI of Table 1, "Applicable Detector" lists the numbers of detector categories (from Table 3) that we judged to be available and suitable for use according to present U.S. Coast Guard requirements. We used data from manufacturers, supplemented in some instances

by our own judgment of the probability that an instrument would or would not detect a given substance at the necessary alarm level. When in doubt, we either put the number of the best-seeming device in parentheses, or we entered "none."

In Column XII, "Applicable Technology," we listed categories (again from Table 3) of techniques that we believe have shown promise of adaptation to the detection of the particular substance given. Some of these entries have been made because the entry from Column XI was "none" or doubtful, due to lack of demonstrated sensitivity of any known device for that substance. In other cases, especially for organic compounds, an entry in Column XII was made to show the possibility of achieving desirable selectivity when more than one detectable vapor might be present.

Recommendations of "Applicable Detector" and "Applicable Technology" were not made for substances listed in Table C-2 of Appendix C because insufficient data were available to permit reliable recommendations to be made for most of these substances.

All of the compounds listed in Table 1 and in Appendix 2, Table C-2, have been assigned to chemical classes, based on a system currently accepted by U.S. E.P.A. for analysis and assessment of environmental pollutants (Cleland 77). Within rather broad and sometimes overlapping categories, applicable detectors and technologies for monitoring of vapors of these compounds correspond to the chemical classes to which the compounds belong. (See Table 2.)

In order to predict with reasonable confidence whether a substance's vapors will be detectable by a given type of sensor, one needs to know, as a minimum, at what concentration the vapors will need to be detected, and what the response of a given sensor is to that kind of substance at that concentration. In the absence of IDLH values for substances in Table C-2, only the existence of TLV Ceiling (C) values represents a possibly valid level of concern. TLV Ceiling values are available for only seven (7) of the compounds in Table C-2. They are listed, together with their TLV(C) values, their chemical classes and suggested applicable detector technologies, in Table 6.

Table 6

Substances from Table C-2 (Appendix 2) Having TLV(C) Values

Chemical Name	Chemical Class	TLV(C)	Available Technology
n-Butylamine	10	5	8
sec-Butylamine	10	5	8
tert-Butylamine	10	5	8
Chlorine Trifluoride	23	0.1	9
Dichloroethyl Ether	24	15	8,9
Methyl Mercaptan	12	10	8
a-Methyl Styrene	14	100	2,5,8

For the remaining compounds in Table C-2, one should be able to identify existing detection capabilities or potentially applicable sensor technology, once the appropriate concentration levels are established, by matching chemical classes with sensitivity characteristics of particular sensors.

Oxygen Deficiency

Several manufacturers now produce personnel monitors that meet U.S. Coast Guard criteria. These devices are well proven in practice and are likely to be acceptable in the future. They are easily integrated with other types of detector systems, but, since they have a highly specific purpose, they are not capable of performing any other needed function. Some examples of commercial devices are listed in Tables 3 and 6.

3. Flammable (Explosive) Limits

A number of commercial devices are available, either as single-purpose units, or as selectable-function monitors (to detect either explosive limits of combustibles or one or more toxic substances such as H₂S or organic vapors), or as components of multi-purpose monitoring systems. Although semiconductor devices (metal oxide gas sensors or the so-called electrolytic sensors) have some limited utility in detection of the relatively high concentrations of vapors associated with flammability in air, the most popular and well-proven devices are the catalytic detectors. In fact, catalytic detectors are mainly useful for measuring concentrations of oxidizable gases in ranges below the lower flammable or explosive limits (LEL or LFL) of those substances in air. For relatively easily oxidizable substances such as hydrocarbons, LEL concentrations are in the range of 0.5-5% by volume in air. The lowest concentration of any gas that can be measured in air is limited by the signal-to-noise ratio of the temperature sensor. Inasmuch as these devices are operated at elevated temperatures, most of the noise is produced by thermal effects and, although these effects can be reduced by proper insulation and by using stabilized power supplies, it is generally not possible to accurately measure concentrations of oxidizable vapors below about 1% of LEL. These detectors are usually calibrated to read "% LEL," and must be adjusted for the actual limit of the material of concern.

Catalytic detectors are relatively nonspecific in their response to combustible (i.e., easily oxidizable) gases and vapors. Virtually all substances in chemical classes 1, 3-12, 14, 16, 17, 19-22, 27 and 28 are detectable at concentrations of concern. (See Table 2.)

The main deficiency of catalytic detectors lies in their susceptibility to interference from certain gaseous substances that are much more strongly adsorbed on the catalyst surface than either the gas to be measured or oxygen. When gases are present, their strong adsorption limits the area of the surface available for reaction of the oxidizable gas of interest and, therefore, reduces the sensitivity of the device. Furthermore, if the interfering molecules are oxidized on the catalyst surface to yield a strongly adsorbed solid product, a cumulative reduction

in surface area occurs which is not reversible, thus effectively poisoning the surface. Although some protection against such "poisoning" might be afforded through the use of semi-permeable membranes as filters to exclude these substances, the technique is not sufficiently selective for general use since membranes tend to differentiate substances mostly on the basis of molecular weight, irrespective of their adsorbability. Although Hopcalite catalysts are satisfactory for use in purification of air contaminated with oxidizable organic substances, they are not commonly used as detection elements, and are judged to be inferior to the platinum filament type of sensor.

Existing monitors for flammable/explosive limits are available in sizes, shapes and weights that are entirely compatible with U.S. Coast Guard criteria for personnel monitoring systems.

4. Toxic Vapors

As indicated in the opening remarks, the area of toxic vapor monitoring, while exhibiting a number of examples of applicable detectors and proven systems, still requires further development. A glance at Column XI of Table 1 shows a large number of 1s and 2s, together with a few 3s, and a few other designations, indicating that for organic vapors in the range of 50-1000 ppm, which is most likely to be the region of U.S. Coast Guard needs, the catalytic detectors and metal oxide semiconductors are widely applicable. In fact, where only a single organic vapor is present, one of these detectors set at the level of concern for toxicity will probably be entirely satisfactory. (Note that toxic levels are almost always lower than flammable limits for the same substance, so that if the action to be taken, pursuant to a warning, is evacuation of the area, the one warning should be sufficient.)

If, however, more than one substance is present, and different alarm levels are appropriate for each of them, then an ability to discriminate and select will be necessary for the detector. With respect to different organic vapors, the detectors in categories 1, 2 and 3 have very little selectivity, and would therefore be limited in their effectiveness under such circumstances.

Unfortunately, very few other types of detectors are now available in forms that meet the design specifications of this study. A surprisingly large number of toxic inorganic vapors and gases, several of them widely used and transported in bulk quantities, are not detectable by existing acceptable devices. Devices that offer some selectivity in addition to high sensitivity, such as infrared adsorption instruments, are still too large and heavy to meet the present needs. Instruments that use separation technology to achieve specificity, such as gas chromatographs, generally require repetitive batch sampling which may result in effective response times that are too long to be acceptable.

The GC system described in Section VIB seems best suited for analysis of vapors of volatile organic compounds in air. These substances could be analyzed repetitively throughout the day and an effective measure of exposure derived. Calibration is achieved through standard analytical procedures, the response factors and relative retention times being stored in a small computer contained within the GC. In this way, concentration and identification of sample components can be verified.

The design characteristics of this "pocket-sized" GC, which make it suitable for utilization in continuous field analysis, also limit its widespread application. The system has a power supply which must be able to operate the GC for a full day on a single charge. This, plus size limitations, preclude the use of heat. Vapors of compounds with high boiling points could therefore not be analyzed.

The use of the thermal conductivity detector is a necessity since a GC worn by working personnel should not utilize flames for safety reasons. The thermal conductivity detector requires only the use of helium carrier gas. The disadvantage of this detector is its relatively low sensitivity. Many compounds have toxic effects at concentrations below the detection limit of this type of detector.

In summary, the shortcomings of the pocket-sized miniature GC are its limited applicability to a wide range of compounds and inadequate sensitivity for high toxic compounds. In addition, separation techniques on this scale are, at present, quite difficult. This limits the instrument's application even further.

The plasma chromatography (PC) technique is applicable only to measurements of trace quantities in the range of 10^{-8} to 10^{-14} grams. In fact, samples containing analyte at higher levels completely saturate the instrument. The instrumentation is theoretically more suitable for field use than is the mass spectrometer because the entire system is small and operates at atmospheric pressure. The ion source and drift tube are on the order of 14 cm in length, although the associated electronic and power supplies add considerable size and weight to the system. A severe limitation to the general applicability of PC to complex samples is the fact that it has relatively poor qualitative resolution. Ions with masses of 42, 52, and 60 show up as a series of three badly overlapped peaks on the plasma chromatography output (Carr 77); the simplest of low resolution mass spectrometers generally provides unit mass resolution. The analytical limitations resulting from the relatively poor qualitative resolution of PC can be greatly ameliorated, as they are in low resolution mass spectrometry, by coupling the PC to a gas chromatograph. While that combination is in fact possible, it takes the PC out of the realm of the real-time instrument and further increases its bulk. Thus, while it is possible that plasma chromatography in conjunction with some specialized gas chromatographic procedures may prove to be the basis of a portable (suitcase-sized) detector for specific, well-suited analytes of particular interest, e.g., TNT, it is doubtful that the instrument can be made sufficiently small, rugged, and reliable to be a general-purpose, portable, toxic gas analyzer.

Chemical ionization devices (specifically the family of instruments currently offered by General Electric Corporation for halogen detection) represent an interesting adjunct to the detectors of Categories 1, 2 and 3. Catalytic and oxidizing semiconductor devices tend to have relatively poor sensitivities to halogen-containing substances, in addition to having little or no specificity to this type of compound as such. The G.E. instruments offer high sensitivity and are specific to the presence of the halogen elements. The pocket-size "Tracker" seems to be a potentially useful personnel monitor for this class of vapors.

Chemical color-forming systems offer perhaps the highest specificity for individual chemical compounds, especially those with characteristic chemical reactivity, such as is exhibited by most inorganic and many reactive organic compounds. Although the basic technology is very old, development of continuous-duty personnel monitors that offer spontaneous audio/video alarm and are continuously sensitive to present concentrations (as distinguished from those that integrate dosage and are useful only for intermittent batch-sampling) has been slow and disappointing. At least one company (MDA Scientific) has recently addressed itself to the present need, and there appears to be some promise of further development of practical devices from this type of technology.

Optical monitors are limited to the detection of mercury vapor (via the ultraviolet) and to a few types of infrared spectrometers for organic compounds. In principle, infrared spectrometry is capable of high selectivity for many organic vapors. Existing portable instruments have tended to sacrifice much of this capability, however, in the interest of attaining other desirable properties for current industrial needs. Lack of adequate wave-length resolution is a typical limitation of the smaller portable instruments, such that, although quantitative measurements may be possible, qualitative discrimination is adversely affected. Instruments have been produced at one time or another that demonstrate the feasibility of achieving good selectivity without sacrificing compactness and portability. Unfortunately, however, no such device is currently available on the commercial market.

The solid-state detectors (Categories 2 and 3) offer many advantages as sensors for toxic vapors and gases and to a limited extent as flammable vapor detectors. Among these advantages are small size, large signal in the presence of low concentrations, and simple signal conditioning circuitry. These properties render miniaturization and incorporation into an integrated device relatively straightforward. Furthermore, the dectors are capable of detecting a wide variety of oxidizable organic and inorganic vapors and gases, such that for applications in which warning is required of the presence of small amounts of any oxidizable vapor or gas the detecto should be quite useful.

On the other hand, non-specificity can be a distinct disadvantage. For example, if a small amount of highly-toxic vapor is present with a substantially larger amount of relatively innocuous gas or vapor, a warning signal will be generated and the appropriate personnel response

must be made. There may be instances, however, when personnel may need to perform work in the presence of the innocuous vapor, but must also be warned if small amounts of toxic vapors or gases are present, hence, some means of obtaining high specificity and sensitivity would be desirable. With a few exceptions, this does not appear to be possible with the present state-of-the-art devices.

Some recent information has become available which indicates some hope. A company called International Sensor Technology has introduced a solid-state sensor which is claimed to have specificity for low concentrations of gases such as H2S and NH3, in the presence of higher concentrations of hydrocarbons. Furthermore, the claim is made that both low (ppm) and high (% LEL) concentrations of gases and vapors can be measured. The manufacturer claims that the sensor element operates on a different principle involving ionic conduction. The claim is made that gases and vapors are ionized by the oxide sensor element, and that by varying the composition and operating temperature, specificity and applicability to a wide concentration range can be obtained. It is interesting to note, however, that some of the compositions and materials revealed are substantially the same as specified for the Taguchi Gas Sensor. Unfortunately, the data supporting the claimed mechanism has been extremely limited. Nevertheless, these devices have been marketed and, for some purposes at least, they appear to work with acceptable reliability.

5. Monitor Combinations

a. Introduction

At the outset of this program, to give us maximum flexibility, we made an assumption that it was quite likely that we would find many different sensors capable of detecting one or more of the substances of interest, but that we would find few, if any, devices composed of combinations of sensors that would meet a significant number of the statements of need developed in Task I. The statements of need included the need to monitor oxygen deficiency, potentially flammable/explosive concentrations and/or toxic levels of chemical substances, as well as the capability to determine the onset of deterioration of the protective suit. Since no transducer capable of sensing suit deterioration was found, that need was set aside for the remainder of this survey. An examination of the list of substances of concern revealed that for a given chemical compound, its hazard would be manifest either by its existence at a level approaching the lower explosive/flammable limit (LEL/LFL) or by its existence at a concentration where it would have toxic effects on spill response personnel. Therefore, assuming that the identity of a spilled substance is known, a minimum device would need to detect oxygen deficiency and either percent LEL/LFL (generally in the range of a few percent by volume) or potentially toxic levels (generally in the lowto mid-ppm range). Because of the particularly disastrous effects of fire and explosion, and because of the possibility that flammable

or explosive substances might also be present at the site of a spill of a substance whose primary impact would be its toxicity, the inclusion of a combustible gas sensor in every device, regardless of the particular substance(s) for which the device was specifically designed, was deemed to be desirable.

b. Available Device Combinations

Contrary to our initial assumption that few, if any, of the statements of need could be met by available devices, our search of available technology revealed that at least four vendors offered devices that had the potential to meet a significant number of the abbreviated (suit integrity eliminated) statements of need. All offered the capability to detect oxygen deficiency and percent LEL/LFL. Two offered the capability to detect lower concentrations of toxic gases either simultaneously with combustible gas measurement or in place of it.

The salient characteristics of the available combination devices are summarized in Table 7. Three of these, the BioM.rine 900, the DynaMation 033, and the Enmet CGS-10 have been recently subjected to extensive testing on behalf of the Coast Guard by the U.S. Bureau of Mines (Chilton, 78). All of the devices, except for the MSA 250, whose weight was not specified, are within the size and weight guidelines set forth by the Coast Guard for this survey. All of the devices feature rechargeable NiCd batteries; readout/warning is by means of a variety of meters, flashing LED lights, or audio alarms. In the areas of battery power and readout warning, the Coast Guard could make substantial improvements in human engineering and reliability; possible initiatives to that end will be discussed later.

All the devices measured oxygen level by the same generic type of electrochemical cell, although the descriptive terminologies differ. Oxygen diffuses through a Teflon R membrane into the cell electrolyte where it reacts with an electrode material to produce a current sufficient to drive a panel meter. Unless thresholding electronics are to be employed or an annunciator is to be driven, the oxygen sensor requires no external power. The cell electrode is consumed during operation, resulting in a finite lifetime for each cell; vendors generally guarantee the life to be at least six months. The cells are filled with a liquid electrolyte, which fact makes them unsuitable for use below 0°C.

All of the devices in Table 7 measure percent LEL/ FL (or other combustible gas concentrations expressed as methane) using either the hot-wire catalytic detector or the solid-state catalytic detector, both of which were described in detail earlier. An important limiting characteristic of certain hot-wire catalytic detectors is exemplified by the BioMarine Model 900 sensor. Because a significant amount of power is required to heat the wire, it is energized for a period of

Integrated Personnel Monitoring Systems Currently Available from Commercial Vendors

Comments	02 is continuous; % LEL measured once every 3 minutes.	02 level is continuous; pushbutton for 2 lel.	. 2 4	cell Can be switched te to high tempera- ture for CH, and other hydro-	carbons.
Transducer	Au/KGH/Pb cell catalytic	Au/KOH/Pb cell catalytic	Electrolytic cell Solid state catalytic Solid state catalytic	Electrochtmical cell Single solid state catalytic	Calvanic call
Response Time (sec)	010	10 5	30 0 0	x.s. (e)	
Substance/ Parameter Measured	o ? LEL	o; Z LEL	05 % LEL CO	ο ₂ LEL <u>or</u> co/H ₂ S	ć
Readout	meter audio/visual	meter	audio/visual	andio/visual	
Power Source/ Operating Time	Nica/+0 hrs.	NICd/400 Comb. readings	NiCd/9 hrs.		Rechargeable/
Dimensions (in)	4 × 8-1/4 × 3	3-1/4 x 7 x 2	4 x 8 x 2-3/4	4-3/4 x 3-3/4 x 2-1/4 NiCd/7-9 hrs.	N.S. 7-1/2 x 5-3/8 x 3-3/8 Rechargeable/
Weight (Ibs)	~	5.5	1.9		
Model	Cor	575	034 (b)	CCS-10	250 ^(d)
Manufacturer	stollarine Industries	Stomarine Industries	DynaNat i on	Ептет	MSA

Notes:

(a) Instrument can be modified to perform a 2 LEL measurement once every 72 sec with a reduction of battery life to 10 hrs.

Calvanic cell catalytic

N.S.

02 2 LEL

meters (d)

N.S. 7-1/2 x 5-3/8 x 3-3/8 Rechargeable/ 8-10 hrs. (b) Also offered as Model 033 Calibrated for H₂S (10 ppm full-scale) instead of CO.

(c) N.S. = Not Specified.

(d) Also available as Model 260 with audio/visual alarm instead of meters.

ten seconds only once very three minutes. However, the measurement frequency can be increased with a resultant increase in power consumption. In the Bureau of Mines tests, the cycle was shortened to a measurement every 72 seconds. At that higher-duty cycle, the battery pack lasted slightly more than eight hours before recharging was necessary. Continuous operation of the hot wire for even two hours would probably require more power than the NiCd pack could deliver.

The Enmet solid-state catalytic sensor measures low levels of toxic gases expressed as carbon monoxide or hydrogen sulfide when operated under normal conditions. By turning a switch which increases the current flow through the device and raises the operating temperature of the device, the sensor can be made to respond to methane and other hydrocarbons to which it is relatively insensitive at lower temperatures. When operated at the higher temperature, the sensor can measure combustible gas concentrations approaching the LFL/LEL. Although the current drain from the battery pack is increased during high-temperature operation, the Enmet NiCd pack is capable of 7 to 9 hours of operation. The DynaMation device uses two separate solid-state catalytic sensors. Either because one sensor has a different composition or is operated differently, one of the sensors responds primarily to toxic gases like CO or H₂S and the other sensor responds to combustible hydrocarbon-type gases to provide an indication of percent LFL/LEL.

c. Other Sensors and Opportunities for Combining Them into New Devices

Devices like the two- and three-sensor combinations described above should be reasonably adequate to meet the needs for spills involving a relatively large proportion of the substances of interest. If development and deployment of devices of that general type is taken as a first step, then it seems reasonable that a logical next step would be to attempt to create new or improved devices by adding additional sensors to the basic device or by replacing a particular sensor with one having different response characteristics. If the new sensor could be made sufficiently similar in terms of size, shape, voltage requirements, and output signal characteristics, a modular system with interchangeable sensors could be envisioned.

After our examination of the present state of the sensor art, we believe several current detector technologies might be adaptable to such a modular approach. The response characteristics of solid-state catalytic sensors are known to change with temperature, and it is likely that they could be altered by changes in device composition as well. It should also be possible to impart selectivity by employing filters which would remove particular interfering substances or classes of substances. The family of sensors that would result should be sufficiently similar so that they could be equipped with a standardized plug which would permit one to be interchanged with another in the device package which contained the power supply, oxygen sensor, and combustible gas detector.

A family of sensors called solid-state electrolytic cell gas sensors which apparently have differing sensitivity and selectivity characteristics are manufactured and marketed by International Sensor Technology. One of their single sensor devices was discussed in the findings related to Task II. While the only means of achieving selectivity that is explicitly discussed in IST literature is the use of a filter, it is likely that changes in selectivity and relative response could also involve changes in device composition and/or operating conditions. The IST portable sensors operate on NiCd batteries; the active sensor elements are quite small; and the gas to be measured is carried to the element by convection. Because of their apparent functional similarity to solid-state catalytic detectors, electrolytic cell gas sensors might be fabricated to be plug-to-plug compatible with the solid-state catalytic sensors.

A third technique which might also be added to a device composed of solid-state sensors or might even be made to be interchangeable with one of the sensors, is the platinum/alkali halide halogenated hydrocarbon detector manufactured by General Electric. That type of sensor has been packaged as a hand-held, battery-powered refrigerant leak detector, so it appears to have the basic characteristics that would make it be compatible with a modular personal monitor. In the evaluations performed in conjuction with Task III, that particular sensor was noted to fill a relatively important gap because of its ability to measure halogenated hydrocarbons which are difficult to measure with many of the other sensors and which tend to temporarily poison some of the hotwire catalytic combustible gas detectors.

Several other potentially useful measuring devices were discussed in conjunction with Task II—paper tape samplers, UV photoionization detectors and infrared spectrometers. Compared to the sensors described above, each of these is sufficiently different from the other two, and from the hot-wire and solid-state sensors described above, that it should probably be viewed as a stand-alone sensor which is used in conjunction with an oxygen/combustible gas monitoring device. Alternatively, any of the three devices could be augmented with the cell required to measure oxygen and a sensor for measuring combustible gases.

d. Opportunities to Improve Usability and Reliability

The combination devices described earlier in the Section employed a variety of means for concentration readout and warning of unsafe conditions. Some utilized meters and other employed various combinations of lights and audio signals. Because the devices were designed to be portable and self-contained, all the audio/visual components were mounted in the device proper. When used in conjunction with a protective suit, the personnel monitor would probably be mounted at or near the backpack where lights could not be seen and alarms not heard. It would thus seem reasonable to envision mounting a small enunciator panel to the rim of the worker's helmet so that color-coded or alpha-

numeric messages were within his field of view as he worked. An audio alert could also be mounted within the helmet to call attention to a warning message on the annunciator panel.

For general personnel monitoring during a work shift, around the work place on a regular day-to-day basis, rechargeable NiCd battery packs are convenient and cost-effective. They can be recharged overnight and are capable of being cycled many times. However, monitors for protecting spill response personnel might lie inactive for extended periods of time until they are needed on the occasion of a spill. At that point, they may need to function for periods of days or even weeks. The rechargeable NiCd battery does not exhibit good charge retention during storage so it would need to be recharged on a regular basis to ensure that it would be in a good state of charge at any particular time. To provide uninterrupted monitoring, extra NiCd packs would need to be available in the field to replace those which had become exhausted.

For this sort of use scenario, a non-rechargeable, primary battery such as the alkaline manganese system may be preferred over rechargeable NiCd's. For a battery of equivalent size and weight, the alkaline manganese system will provide about 1.5 times the energy available from the NiCd system. Alkaline manganese cells also have much better shelf-life characteristics compared to the charge-retention properties of NiCd cells.

Even higher energy densities are available with lithium primary cells which are now becoming commercially available. Lithium "D" cells are available which will deliver in excess of 10 ampere-hours at about 2.9 volts.

VII. GENERAL CONCLUSIONS

A. CAPABILITIES AND LIMITATIONS OF PRESENTLY-AVAILABLE DEVICES

Summarizing the results reported in Sections VI, B, C and D above, we find that personnel monitoring devices are currently available which meet the Coast Guard's stated needs in two categories, oxygen deficiency and flammable limits, and for some substances, in the third category, toxic vapors. We found nothing whatever resembling a solution to the stated need for a device to warn the wearer of protective garments that his equipment is about to fail because of chemical attack.

The principal limitations of existing devices and technologies are most apparent in the area of toxic vapor monitoring. Existing personnel monitors are limited to a few types that are nonspecific detectors for oxidizable organic compounds, and a very few others that are suitable for detection of specific compounds. The nonspecific detectors are unable to select one substance out of a number that might be present at detectable levels. Rather, they simply integrate the effect of all detectable substances. Thus, if several substances having different levels of concern are present in the same atmosphere, these detectors will sense the sum of their concentrations and will be unable to select one that has high toxicity in the presence of other more innocuous species.

Serious gaps in capability occur for some organic substances that have very low toxic limits and for a number of inorganics, irrespective of concentration. Detectors that have the capabilities for additional sensitivity and/or selectivity have not yet been reduced to size, weight and power limitations that are associated with personnel monitors. This, in our opinion, is the area requiring the most urgent attention.

Once an adequate array of individual monitors are available to cover the principal toxic vapors that are likely to be encountered, integration of several monitors into a single package should be possible.

Transducers based on the solid state catalytic and electrolytic principles, and perhaps the platinum alkali halide detector, as well, are quite similar in size and mode of operation. Power to heat the element is required and a measuring potential must be applied across the device.

Adding additional transducers of that sort to a device should be rather straightforward. In fact, it might be possible to mount the transducer in a small housing equipped with a plug so that different transducers could be plugged into a common monitor that would contain the power supply, oxygen sensor and combustible gas detector.

Other measuring devices such as paper tape samples, UV photoionization detectors, and UV/visible/infrared spectrometers are sufficiently different from each other and from the family of solid state sensors to make substantial integration difficult. They would probably be deployed

as a stand-alone sensor, perhaps physically connected to an oxygen/combustible gas monitor and sharing a common battery pack and annunciation system.

B. OPPORTUNITIES FOR IMPROVEMENT OF EXISTING DEVICES

The need for extended monitoring capabilities we have identified could be satisfied in some degree by incremental advances in the performance of existing devices. For instance, keeping in mind the important fact that concentration limits for short-term exposure (the IDLH) to most toxic gases are generally many times higher than the limits set for continuous exposure (the TLV), the published sensitivity of some detectors (photoionization, infrared, chemical ionization) may be more than is needed for the Coast Guard's purposes. Even the widely effective semiconductor detectors have published sensitivity values below those required here. What is needed for these devices is some compromise in characteristics that will be designed around U.S. Coast Guard needs. Furthermore, much more detailed evidence is needed for effects of interferences such as moisture and other gases, and extremes of temperature.

Miniaturization of devices that will afford some selectivity will be an important compromise for devices, such as infrared spectrophotometers. Again, design of these devices around the U.S. Coat Guard's needs would probably show that much can be done in this beneficial direction. Some examples of opportunities for improvement of solid-state detectors are as follows.

1. Piezoelectric Detectors

Coated piezoelectric crystals have become increasingly useful in recent years for the detection of traces of toxic atmospheric pollutants. The detection of a specific atmospheric gas is observed as a change in the resonant frequency of the crystal as a result of selective adsorption by the coating.

Alpha quartz is the most widely used material for piezoelectric crystal detectors. The properties which make it suitable are its water-insolubility and its resistance to temperatures up to 579°C with no loss of piezoelectric properties.

Sauerbrey, in studying the properties of quartz crystals coated with thin metal films, developed a relationship between the mass of a foreign substance and the frequency of a crystal vibrating when an electric field is applied. The relationship for quartz is:

$$\Delta F = 2.3 \times 10^6 \text{ F}^2 (\Delta M_s/\Lambda)$$

where ΔF = the change in frequency due to the coating (Hz), F = the frequency of the quartz plate (MHz), ΔM = mass of deposited coating (g), ΔF = area coated (cm²). The equation is applicable when a gas or vapor is absorbed on a crystal that has been coated with a material that will preferentially sorb the gas.

The advantages of the coated piezoelectric detector include extreme sensitivity to small weight changes ($\sim 10^{-12}$ g), selectivity, attainable through the use of appropriate adsorbent coatings, ruggedness and the potential for miniaturization.

Except for devices for the detection and measurement of water vapor, no commercial instruments are yet available. A possible reason for this is that it is very difficult to find coatings which have long lifetimes, are selective, give a measureable response, do not suffer considerable interferences from other gases and vapors, particularly water vapor, and which are completely reversible.

In Table 8 are listed coatings that have been tried and the gases or vapors for which there is good sensitivity. (Hlarny 77).

2. Schottky Barrier or n-p Junction Devices

Two devices have been described which are based upon the behavior of an n-type semiconductor and a metal rectifying contact. In one embodiment, CdS forms a direct rectifying or barrier contact with a thin layer of metal while the other embodiment involves an MOS structure, i.e., a thin oxide layer (SiO₂) separates the semiconductor (silicon) from the metal (palladium). In both instances, the net result is a rectifying contact. Figure 4 depicts the energy band picture corresponding to each embodiment.

With CdS the rectifying behavior is determined by the relative positions of the metal work function and CdS electron affinity on the energy scale. As Pd has a relatively high work function, the contact with CdS is rectifying rather than ohmic. When $\rm H_2$ is present in the atmosphere, however, the Pd adsorbs the gas and if the Pd layer is thin enough, the $\rm H_2$ diffuses to the CdS-Pd interface, resulting in a change in metal work function. The effect of this on the current-voltage characteristics is shown in Figure 5. This change can be detected as an increase in current flow in the reverse direction.

In the metal oxide semiconductor devices, the mechanism is essentially the same as that outlined for CdS, except that the quantity measured is the "threshold voltage" which is directly related to the metal work function.

Both of these detectors appear to be highly specific for $\rm H_2$ and perhaps for lower hydrocarbons such as $\rm CH_4$. It is conceivable that specificity could be built in for other metal-semiconductor combinations.

C. OUTSTANDING UNSATISFIED REQUIREMENTS

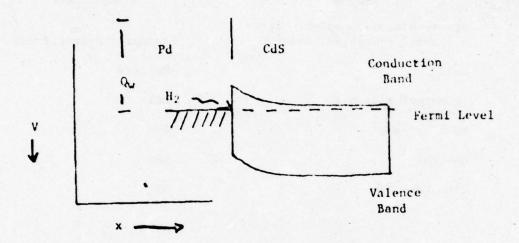
Probably the most dramatic of the unsatisfied requirements is that for a device to warn the individual of impending failure of his protective equipment. While it is clearly impossible to detect the proximity of a hazardous substance, its presence and its initial effects can certainly be detected. On the assumption that attack of clothing and equipment such as gloves, face-mask or boots, would occur at a relatively slow rate, one might apply an outer layer of "sacrificial" material which would show the effect of deterioration by a pronounced change in color

Table 8

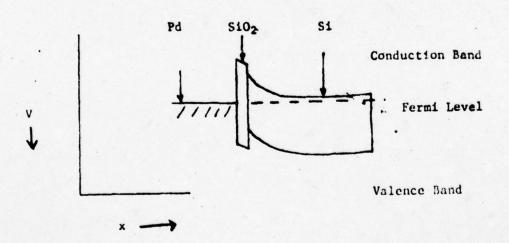
Coatings For Piezoelectric Detectors (Hlarny 77)

Coating	Gas or Vapor	
trans-chlorocarbonyl-bis (tri- phenyl phosphine) iridium	Aromatic hydrocarbons	
Gold	Mercury	
trimethylamine-HCl	HC1	
Soot extract	H ₂ S	
Quadrol	SO ₂	
Ucon LB-300x	NH ₃	

Figure 4
Rectifying Barrier Devices



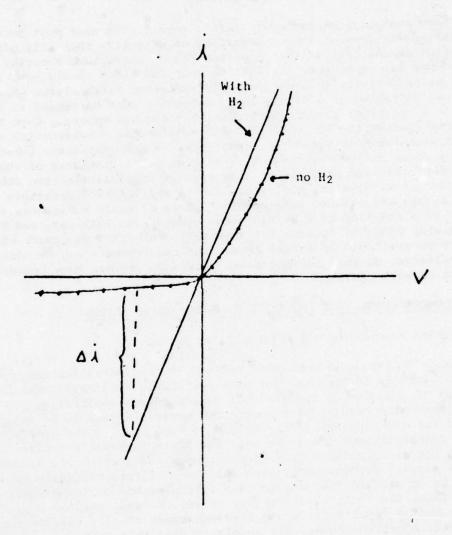
a. Schottky Barrier CdS-Pd Datector



b. MOS Detector

Figure 5

Effect of H₂ Gas on I-V Characteristics of Schottky Barrier Device



or other physical appearance. Soles of boots might be equipped with an intermediate layer of electrical wiring, which if interrupted would cause an open-circuit alarm. Alternatively, two closely spaced systems of wiring or sheet-form conductor might be used as a capacitor, such that swelling (or shrinking) of the matrix would be detected as a change in capacitance.

Punctures could be detected by the simple expedient of loss of pressure if the suit were totally encapsulating and maintained at a slight positive pressure. As far as we have been able to determine, these ideas are entirely the result of our own speculation and have never been reduced to practice for this purpose.

As we have emphasized repeatedly in this report, the next most outstanding unsatisfied requirement is for a variety of detectors that will afford protection against all of the important toxic vapors that a strike team member may encounter. We believe that detectors should have some degree of selectivity in order to avoid excessive false alarms when a small concentration of a highly toxic substance must be sensed in the presence of equal or larger quantities of innocuous vapors. Even when evaluated against the 400 CHRIS Phase I substances, a substantial number of gaps were found in detection capability. Since many toxic substances that may occur in the environment of an accidental discharge of chemicals may be ones that are produced by some sort of chemical reaction due to fire, contact with water, air, etc., the capabilities of detectors should be checked against more complete lists of toxic substances such as have been compiled by U.S. NIOSH and others. In this way, and by knowing what kinds of options for practical protective equipment will actually be available to strike teams, the requirements can be made more realistic, so that designers and manufacturers can have better criteria to work against.

D. RECOMMENDATIONS FOR FURTHER U.S. COAST GUARD ACTION

Develop reasonable and relatistic criteria.

The types of substances to be detected and the concentration range at which an alarm is to be given for each one should be identified. The frequency of measurement required for discontinuous monitoring, and the response time required for continuous monitoring should be determined. The need for substance-specifity should be evaluated. The question of what concentrations should be used for alarm thresholds implies the need for description of the circumstances under which the alarm would be given. For instance, with the XM-41 filter, virtually no barrier is created to the passage (i.e., inhalation) of any organic vapor. Thus, the toxic vapor monitor serves the same purpose as if the user had no respiratory protective equipment at all. If, on the other hand, a self-contained air supply is used in a totally-encapsulating suit, much higher concentrations may be tolerated (depending on U.S. Coast Guard policy) outside the suit, and only much lower ones inside.

2. Expand the variety of practical detection devices available for toxic vapors. This would include both the development of new sensors for substances that are not presently detectable (see Table 9) and the improvement of selectivity of existing sensors that have broad sensitivity to organic vapors.

As the range of <u>miniature</u> toxic vapor detectors available today is inadequate to meet the Coast Guard's needs, we recommend that the Coast Guard initiate action that would result in the expansion of the variety of practical detection devices. The action taken will probably have to include basic and applied research and advanced development.

The area in which the <u>basic</u> research efforts would prove most fruitful is in gaining an understanding of the effects of vapors on the electrical properties of both semiconducting solids and solid ionic conductors. It is with this type of understanding that the way may be found to impart specificity as well as improved sensitivity to existing devices.

As an example, consider the work cited earlier on the Schottky barrier (CdS-Pd) detectors. The limited data available indicate that these detectors are highly specific for $\rm H_2$ gas. It is conceivable that combinations of other semiconductors and metals could be found that would result in similar specificity for other gases and vapors. Furthermore, a combination such as semiconductor/ionic conductor/metal, may have properties that would impart desirable specificity.

Another example is the work being conducted at Arthur D. Little, Inc., on strontium-doped lanthanum cobaltite. We have discovered that this material is highly specific for CO gas under one set of conditions, but appears to be specific for NO under another set of conditions.

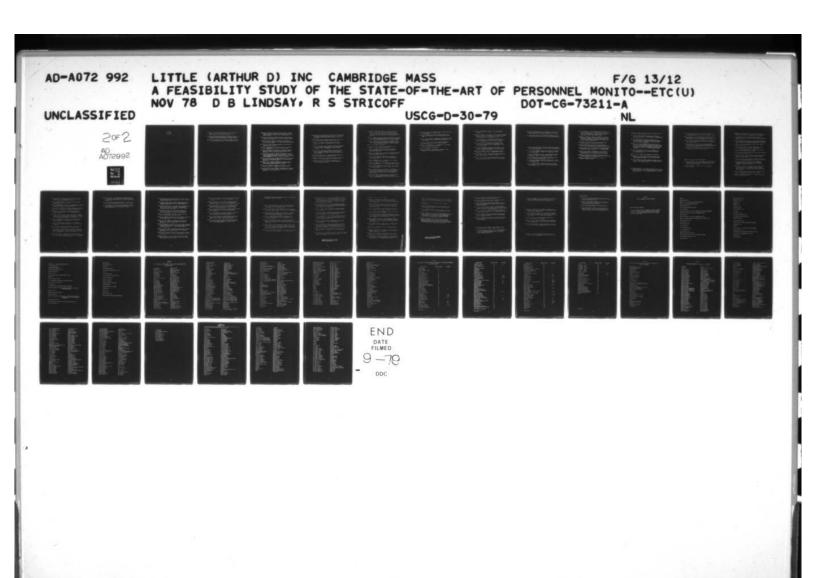
With respect to applied research, an area that appears to be most important is in developing a variety of coatings for the piezo-electric detectors. Finding such a material would be invaluable as we have already noted the high sensitivity of these devices, and miniaturization has already been accomplished. We envision an applied research program in which the sorption and desorption properties of a variety of polymer and film materials is systematically measured. This should lead to the discovery of materials that are 1) reversible and 2) exhibit specificity.

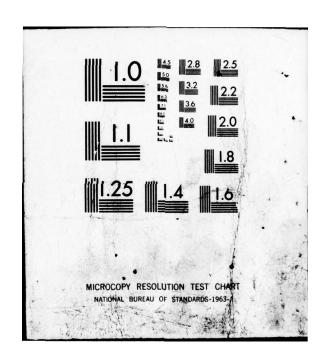
As for advanced development, the most urgent need is for the of miniature versions of the optical devices (IR, UV) and mass spectrometric devices. This type of activity would probably yield the greatest short-term benefits with respect to expanding the variety of practical detection devices as these devices are already capable of high specificity and sensitivity.

High-Priority Hazardous Vapors for Which No Satisfactory
Detector is Currently Available

CHRIS		Chemical	Applicable
Code	Chemical Name	Class (1)	Technology (2)
BRX	Bromine	23	7,9
BZC	Benzoyl chloride	15	9
CBT	Carbon tetrachloride	2	2,7,9
CCL	Cyanogen chloride	23	7,9
CHD	Chlorohydrins (crude)	2	9
CSA	Chlorosulfonic acid	14	9
DSF	Dimethyl sulfate	13	5,7,8
ETI	Ethyleneimine	10	7,8
FMS	Formaldehyde solution	6	5,7
FXX	Fluorine	23	3,9
HCL.	Hydrochloric acid	23	7,9
HDC	Hydrogen chloride	23	7,9
HDZ	Hydrazine	23	7,2
HFX	Hydrogen fluoride	23	7,9
HPO	Hydrogen peroxide	23	(3)
MPΛ	Monoisopropanolamine	10	8
NAC	Nitric acid	23	7
NOX	Nitrogen tetroxide	23	7
NTC	Nitrosyl chloride	23	9
PNA	Propionic acid	7	8
PPO	Phosphorus oxychloride	23	7,9
PPT	Phosphorus trichloride	23	7,9
SFM	Sulfur monochloride	23	9
TCF	Trichlorofluoromethane	2	9
TEL	Tetraethyl lead	23	8
TML	Tetramethyl lead	23	8
VAM	Vinyl acetate	8	8
VCT	Vinylidene chloride (inhibited)	2	8,9

- 3. Probably in connection with the development of protective equipment itself, initiate development of built-in sensors to give warning of insipient failure or loss of integrity.
- 4. Assess plug-to-plug and chassis-to-chassis compatability of different brands, types and styles of detectors, to encourage manufacturers to provide integrated capabilities in single, multifunctional personnel monitoring systems.





APPENDIX A

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APPENDIX B

SOURCES OF COMMERCIAL PRODUCT INFORMATION

Commercial Product Literature

In researching the availability of commercial products, we contacted the following companies. In most instances, we received product literature. In some instances, however, responses were negative indicating an absence of appropriate information, or no response has been received to date.

Abcor Inc.

American Cyanamid Co.

Analabs, Inc. (A subsidiary of New England Nuclear)

Analytical Instrumental Development, Inc.

Anderson Samplers, Inc.

Anti-Pollution Technology Corporation

Aromil Chemical Co.

Atmospheric Sciences, Inc. (ASI no longer makes gas sampling equipment)

Bacharach Instrument Co. (Division of AMBAC Industries)

Barnebey-Cheney

Beckman Instruments Inc. (Process Instruments Division)

Bendix Environmental & Process Instruments Division (Bendix Corp.)

Bio-Marine Industries Inc.

Brailsford & Co., Inc.

Brothers Chemical Co.

E. D. Bullard Co.

Carle Instruments, Inc.

C. F. Casella & Co. Ltd.

Century Systems Corp.

Combustion Equipment Associates

Curtin Matheson Scientific (A Coulter Subsidiary Company)

Davis Emergency Equipment Co., Inc.

Deco Systems, Inc.

Del Mar Scientific, Inc.

Devco Engineering Inc.

Dorr-Oliver, Inc.

Drägerwerk A.G.

Dynamation, Inc.

Dynasciences Corp.

Edax International, Inc.

Enmet Corp.

EnviroMetrics, Inc.

Environmental Compliance Corp.

Environmental Sciences Associates

ERDCO Engineering Co.

Figaro Engineering, Inc.

Flotronics Division (Sales Corporation of America)

Foxboro/Wilks, Inc.

GCA Corp.

General Electric Co. (Instrument Products Operation)

General Monitors, Inc.

General Motors Corp. (Detroit Diesel Allison Division)

Gessellschaft Fur Geratebau Mbtl. & Co. KG

Hach Chemical Co.

Harvard Apparatus

Honeywell, Inc. (Systems & Research Center)

Inax Instruments Ltd.

Instrument Development Co.

The International Nickel Co., Inc.

Kem-Tech Laboratories

Kontes Glass Co.

Lumidor Safety Products (Lumidor Products Corp.?)

Magna Corp.

McMillan Electronics Corp.

Meloy Laboratories (Instruments and Systems Division)

John P. Mickel Associates, Inc.

Millipore Corp.

Mine Safety Appliances (and MSA Research Corporation)

Misco/Sierra Products (formerly Flowmaster Products Inc. and Sierra Weather Instruments)

Monitor Labs Inc.

Monsanto Enviro-Chem Systems Inc.

National Draeger Inc.

National Environmental Instruments, Inc. (formerly Union Industrial Equipment Corp. and Unico Environmental Instruments)

National Mine Service Co.

The Pace Companies (subsidiary of Jacobs Engineering Group, Inc.)

John A. Pendergrass Co.

Photovolt Corp.

Pope Scientific, Inc.

Reiss Corp.

Research Appliance Co.

Riken Keiki Fine Instrument Co., Ltd.

SKC, Inc.

Scientific Industries

Scott Aviation Division (A-T-O Inc.)

Sensor Technology, Inc.

Anatole J. Sipin Co.

Soap Film Flowmeter

Sunshine Scientific Instruments

Taft Laboratories

Teledyne Analytical Instruments

Tintometer Ltd.

Tracor, Inc.

Whittaker Corp.

Wilks Scientific Corp.

Willson Products Division (ESB Incorporated)

APPENDIX C TABLE C-1

CHRIS COMPOUNDS FOR WHOSE VAPORS THE XM-41 FILTER IS NOT CONSIDERED AN EFFECTIVE BARRIER

Acetaldehyde Acetic Acid Acetic Anhydride Acetone Acetone Cyanohydrin Acetonitrile

Acetophenone Acetylacetone Acetyl Bromide Acetyl Chloride Acetylene

Acetyl Peroxide Solution

Acrolein Acrylic Acid Acrylonitrile Allyl Alcohol Allyl Bromide Allyl Chloride Allylchloroformate Allyl Trichlorosilane Ammonia Anhydrous Ammonium Sulfide Amyl Acetate (n-) Amyl Alcohol (n-) Amyl Chloride (n-)

Amyl Methyl Ketone (n-) Amylnitrate (n-) Amyl Nitrite (iso-)

Amyl Mercaptan (n-)

Aniline

Antimony Pentachloride Antimony Pentafluoride Antimony Trichloride Arsenic Trichloride

Asphalt Blending Stocks: ROC

Benzaldehyde Benzene

Benzene Phosphorus Dichloride

Benzene Phosphorus Thiodichloride

Benzonitrile Benzovl Chloride Benzylamine Benzyl Bromide Benzyl Chloride Boron Trichloride Boron Tribromide

Bromine

Bromine Pentafluoride Bromine Trifluoride

Bromobenzene

Butadiene, Inhibited

Butane

1,4-Butanediol 1,4-Burenediol Butyl Acetate (n-) Butyl Acetate (sec-) Butyl Acrylate (iso-) Butyl Acrylate (n-) Butyl Alcohol (n-) Butyl Alcohol (sec-) Butyl Alcohol (tert-)

Butylamine (n-) Butylamine (sec-) Butylamine (tert-) Butylene (Gas) 1,2-Butylene Oxide

Butyl Hydroperoxide (tert-)

Butyl Mercaptan (n-) Butyltricholorsilane Butyraldehyde (n-) Butyraldehyde (iso-) Butyric Acid (n-)

Camphene Camphor (0il) Carbolic Oil Carbon Dioxide Carbon Disulfide Carbon Monoxide

Carbon Tetrachloride

Carene Chlorine

Chlorine Trifluoride Chloracetyl Chloride

Chlorobenzene

4-Chlorobutyronitrile

Chloroform

Chlorohydrin (Crude) Chloromethyl Methyl Ether

Chlorophenol (p-) Chloropicrin (Liquid) Chlorosulfonic Acid Chromyl Chloride

Cresols

Cresyl Glycidyl Ether

Crotonaldehyde

Cumene Cyanogen

Cyanogen Bromide Cyanogen Chloride

Cyclohexane Cyclohexanol Cyclohexanone

Cyclohexanone Peroxide

Cyclohexylamine Cyclopentane Cyclopropane Cymene (p-) Decaldehyde 1-Decene

Diacetone Alcohol
n-Dibutylamine
n-Dibutyl Ether
n-Dibutyl Ketone
Dichlorobenzene (o-)
Dichlorobenzene (p-)

Dichlorobutene

Dichlorodifluoromethane 1,2-Dichloroethylene Dichloroethyle Ether Dichloromethane 2,4-Dichlorophenol

1,2-Dichloropropane Dichloropropene

1,1-Difluoroethane 1,1-Dimethylhydrazine

Dicyclopentadiene Diethylamine Diethylbenzene Diethyl Carbonate

Diethylene Glycol Dymethyl Ether Diethylene Glycol Monoethyl Ether Diethylene Glycol Monomethyl Ether

Diethylenetriamine

Diethylzinc

Difluorophosphoric Acid, Anhydrous

Diisobutyl Carbinol Diisobutylene

Diisobutyl Ketone Diisopropanolamine

Diisopropylamine Diisopropylamine

Dimethylacetamide

Dimethylamine Dimethyl Ether

Dimethyldichlorosilane

Dimethylformamide Dimethyl Sulfate Dimethyl Sulfide Dimethyl Sulfoxide

Dimethylzinc
Dioxane (1,4-)
Dipentene

Di-N-Propylamine

Distillates: Flashed Feed Stocks

Distillates: Straight Run

1-Dodecene Dodecene Epichlorohydrin

Ethane

Ethyl Acetate Ethyl Acetoacetate Ethyl Acrylate Ethyl Alcohol

Ethylaluminum Dichloride Ethylaluminum Sesquichloride

Ethylamine
Ethylbenzene
Ethyl Butanol
Ethyl Butyrate
Ethyl Chloride
Ethyl Chloroacetate
Ethyl Chloroformate
Ethyl Dichlorosilane

Ethylene

Ethylene Chlorohydrin

Ethylenediamine
Ethylene Dibromide
Ethylene Dichloride

Ethylene Glycol Diacetate
Ethylene Glycol Diethyl Ether
Ethylene Glycol Dimethyl Ether
Ethylene Glycol Monobatyl Ether
Ethylene Glycol Monoethyl Ether
Ethylene Glycol Monoethyl Ether

Acetate

Ethylene Glycol Monomethyl Ether

Ethyleneimine
Ethylene Oxide
Ethyl Ether
Ethyl Formate
Ethylhexaldehyde
2-Ethyl Hexanol

2-Ethylhexyl Acrylate, Inhibited

Ethylidenenorbornene

Ethyl Lactate Ethyl Mercaptan Ethyl Methacrylate Ethyl Nitrite

Ethylphenyldichlorosilane

Ethyl Phosphonothiodic Dichloride,

Anhydrous

Ethyl Phosphorodichloridate 2-Ethyl-3-Propylacrolein

Ethyl Silicate

Ethyltrichlorosilane

Fluorine Furfural

Gas Oil: Cracked
Gasoline: Automotive
(4.23G PB/Gal)

Gasoline: Casinghead
Gasoline: Polymer
Gasoline: Straight Run

Gasoline Blending Stocks: Alkylates
Gasoline Blending Stocks: Reformates

Glyoxal, 40 (Solution)

Heptane Heptanol 1-Heptene

I-Hexaldehyde (n-)
Hexamethylenediamine
Hexamethyleneimine

Hexane Hexanol 1-Hexene

Hydrogen Peroxide Hydrogen Sulfide

2-Hydroxyethyl Acrylate, Inhibited

Hydroxypropyl Acrylate Hydroxypropyl Methacrylate

Isoamyl Alcohol Isobutane

Isobutyl Acetate
Isobutyl Alcohol
Isobutylamine
Isobutylene
Isobutyric Acid
Isobutyronitrile
Isodecaldehyde

Isodecyl Acrylate, Inhibited

Isohexane Isooctaldehyde Isooctyl Alcohol

Isopentane

Isophorone Isoprene

Isopropyl Acetate
Isopropyl Alcohol
Isopropylamine
Isopropyl Ether
Isopropyl Mercaptan
Isovaleraldehyde

Jet Fuel: JP-1 (Kerosene)

Jet Fuel: JP-3 Jet Fuel: JP-4

Jet Fuel: JP-5 (Kerosene, Heavy)

Liquified Natural Gas Liquified Petroleum Gas

Maleic Anhydride

Mercury Mesityl Oxide Methallyl Chloride Methane

Methyl Acetate

Methyl Acetylene-Propadiene Mixture

Methylacrylate Methyl Alcohol Methylamine

Methyl Amyl Acetate Methyl Amyl Alcohol Methylaniline (n-) Methyl Bromide Methyl-n-Butyl Keton

Methyl-n-Butyl Ketone Methyl Chloride Methyl Chloroformate Methylcyclopentane Methyl Dichlorosilane Methyl Ethyl Ketone Methylethylpyridine

Methyl Formal Methyl Formate Methyl Hydrazine

Methyl Isobutyl Carbinol Methyl Isobutyl Ketone

Methyl Isopropenyl Ketone, Inhibited

Methyl Mercaptan Methyl Methacrylate

Methylphospho othioic Dichloride,

Anhydrous

Methylstyrene, Alpha Methyltrichlorosilane Methyl Vinyl Ketone Mineral Spirits

Oil Fuel: No. 1 (Kerosene) Monochloroacetic Acid 011 Fuel: No. 1-D Monochlorodifluoromethane Monoethanolamine Oil Fuel: No. 2 Monoisopropanolamine 011 Fuel: No. 2-D 011 Fuel: No. 4 Morpholine Motor Fuel Antiknock Comp. Oil Fuel: No. 5 Naphtha: Coal Tar Oil Fuel: No. 6 Naphtha: Solvent Oil Misc: Absorption Oil Misc: Coal Tar Naphtha: Stoddard Solvent Naphtha: VM + P (75 Naphtha) Oil Misc: Croton Naphthalene, Molten Oil Misc: Linseed Naphthenic Acid Oil Misc: Lubricating Oil Misc: Mineral Neohexane Oil Misc: Mineral Seal Nickel Carbonyl Nitric Acid Oil Misc: Motor Oil Misc: Neatsfoot Nitric Oxide Oil Misc: Penetrating Nitrobenzene Oil Misc: Range Nitroethane Nitrogen, Liquified Oil Misc: Resin Oil Misc: Road Nitrogen Tetroxide Oil Misc: Rosin Nitromethane Oil Misc: Sperm 2-Nitrophenol Oil Misc: Spindle 4-Nitrophenol Oil Misc: Spray 2-Nitropropane Oil Misc: Tall Nitrosyl Chloride Oil Misc: Tanner's Nitrous Oxide Oil Misc: Transformer Nonane 011 Misc: Turbine Nonene 1-Nonene Oxygen, Liquid Paraformaldehyde Octane Pentaborane Octano1 Pentane 1-Octene 1-Pentene Oil: Clarified Paracetic Acid Oil: Crude Perchloromethyl Mercaptan Oil: Diesel Oil Edible: Castor Petroleum Naphtha Pheno1 Oil Edible: Coconut Oil Edible: Cottonseed Phosgene Oil Edible: Fish Phosphorus Tribromide Oil Edible: Lard Phosphorus Trichloride Piperazene Oil Edible: Olive Oil Edible: Palm Propane Propiolactone, Beta Oil Edible: Peanut Oil Edible: Safflower Propionaldehyde Oil Edible: Soya Bean Propionic Acid Propionic Anhydride Oil Edible: Tucum

Propyl Acetate (n-)

Oil Edible: Vegetable

Propyl Alcohol (n-) Propylene Propylene Glycol Propylene Glycol Methyl Ether Propyleneimine, Inhibited Propylene Oxide Propylene Tetramer Propyl Mercaptan (n-) Pyridine Silicon Tetrachloride Styrene Sulfur Dioxide Sulfur Monochloride Sulfuryl Chloride Tetrachloroethane Tetrachloroethylene Tetraethyl Lead Tetrafluoroethylene Inhibited Tetrahydrofuran Tetrahydronaphthalene Tetramethyl Lead Thiophosgene Titanium Tetrachloride Toluene Toluidene (o-) Trichloroethane Trichloroethylene Trichlorofluoromethane Trichlorosilane Triethylamine Triethylbenzene Trifluorochloroethylene Triisobutylaluminum Trimethylamine Trimethylchlorosilane Turpentine 1-Undecene Valeraldehyde Vanadium Oxytrichloride Vinyl Acetate Vinyl Chloride Vinyl Fluoride, Inhibited Vinylidene Chloride, Inhibited Vinyl Methyl Ether, Inhibited Vinyl Foluene Vinyl Trichlorosilane Xylene (m-) Xylene (o-) Xylene (p-) Xylenol

Table C-2

CHRIS PHASE II SUBSTANCES FOR WHOSE VAPORS THE XM-41 FILTER IS NOT CONSIDERED

AN EFFECTIVE BARRIER

Chemical Name	Chemical Class*	TLV (ppm)
Acetylacetone	6	
Acetyl Bromide	2	
Acetyl Chloride	2	
Acetyl Peroxide Solution	5	The Train
Acrolein	6	0.1
Allyl Bromide	2	
Allychloroformate	2	the architecture
Allyl Trichlorosilane	2	
Ammonium Sulfide	23	
Amyl Chloride (n-)	2	
Amyl Mercaptan (n-)	12	
Amyl Methyl Ketone (n-)	6	
Amyl Nitrate (n-)	1	
Amyl Nitrite (iso-)	1	
Antimony Pentachloride	23	
Antimony Pentafluoride	23	
Antimony Trichloride	23	
Arsenic Trichloride	23	
Benzene Phosphorus Dichloride	2	
Benzene Phosphorus Thiodichloride	. 2	
Benzonitrile	9	
Benzylamine	10	
Benzyl Bromide	15	
Benzyl Chloride	15	1.0
Boron Trichloride	23	
Boron Tribomide	23	
Bromide Pentafluoride	23	
Bromine Trifluoride	23	
Bromobenzene	15	
Butylamine (n-)	10	5 (c)
Butylamine (sec-)	10	5 (c)
Butylamine (tert-)	10	5 (c)
1,2-Butylene Oxide	5	
Butyl Mercaptan (n-)	12	10
Butyltrichlorosilane	2	
Butyric Acid (n-)	. 7	
Camphene	1	
Carbon Dioxide	23	5000
Carbon Monoxide	23	50
Carene	1	
Chlorine Trifluoride	23	0.1 (c)
Chloracetyl Chloride	2	
4-Chlorobutyronitrile	2	
Chloromethyl Methyl Ether	2	

^{*}See Table 2

Chemical Name	Chemical Class*	TLV (ppm)
Chlorophenol (p-)	18	
Chloropicrin (Liquid)	23	0.1
Chromyl Chloride	23	
Cresyl Glycidyl Ether	3	
Cyanogen	23	
Cyclohexanone Peroxide	5	
Cyclopentane	1	
Cyclopropane	1	
Cymene (p-)	14	
Dibutylamine (n-)	10	
Dibutyl Ether (n-)	3	
Dibutyl Ketone (n-)	6	
Dichlorobutene	2	
1,2-Dichloroethylene	2	200
Dichloroethyl Ether	24	15 (c)
1,1-Difluoroethane	2	
1,1-Dimethylhydrazine	11	0.5
Diethylzine	23	
Difluorophosphoric Acid, Anhydrous	23	
Disobutyl Ketone	6	50
Diisopropylamine	10	5
Dimethylacetamide	8	10
Dimethyl Ether	3	
Dimethyldichlorosilane	23	
Dimethyl Sulfide	12	
Dimethylzinc	23	
Dipentene	1	
Dipropylamine (n-)	10	
Ethylaluminum Dichloride	23	
Ethylaluminum Sesquichloride	23	
Ethylamine	10	10
Ethyl Butyrate	8	
Ethyl Chloroacetate	2	
Ethyl Chloroformate	2	
Ethyldichlorosilane	23	
Ethylene Chlorohydrin	2	5
Ethylene Glycol Diacetate	8	
	3	
Ethylene Glycol Diethyl Ether Ethyl Formate	8	100
	6	100
Ethylhexaldehyde	8	
2-Ethylhexyl Acrylate, Inhibited	2	
Ethylidenenorbornene	8	
Ethyl Lactate		
Ethyl Mercaptan	12	
Ethyl Methacrylate	8	
Ethyl Nitrite	16	etermologies Elley
Ethylphenyldichlorosilane	23	, 1
Ethyl Phosphonothiodic Dichloride, Anhydrous	29	1)1
Ethyl Phosphorodichloridate	29	

^{*}See Table 2

Chemical Name	Chemical Class*	TLV (ppm)
Ethyl Silicate	8	I material of the latest
Ethyltrichlorosilane	23	
Hexaldehyde	6	
Hexamethylenediamine	10	PTOMP TABLES
Hexamethyleneimine	10	
2-Hydroxyethyl Acrylate, Inhibited	8	
Hydroxypropyl Acrylate	8	
Hydroxypropyl Methacrylate	8	
Isobutyric Acid	7	
Isobutyronitrile	9	
Isodecyl Acrylate, Inhibited	8	
Isophorone	6	25
Isopropylamine	10	5
	3	500
Isopropyl Ether	12	Literatura (Cas Cas Cas Cas Cas Cas Cas Cas Cas Cas
Isopropyl Mercaptan	6	se rock later of
Isovaleraldehyde	6	25
Mesityl Oxide	2	THE SALVATORS
Methallyl Chloride	8	200
Methyl Acetate	1	1000
Methyl Acetylene-Propadiene Mixture	10	10
Methylamine	10	10
Methylaniline	6	100
Methyl Butyl Ketone	2	100
Methyl Chloroformate		
Methyl Cyclopentane	1 23	
Methyl Dichlorosilane		100
Methyl Formal	6	100
Methyl Formate	8	
Methyl Hydrazine	11	
Methyl Isopropenyl Ketone, Inhibited	1 6	10 (c)
Methyl Mercaptan	12	10 (0)
Methylphosphonothioic Dichloride, Anhydrous	29	
Methylstyrene, alpha-	14	100 (c)
Methyltrichlorosilane	23	
Methyl Vinyl Ketone	6	
Monochloroacetic Acid	2	
Naphthalene, Molten	20	10
Naphthenic Acid	14	
Neohexane	1	
Nickel Carbonyl	23	0.001
Nitric Oxide	23	25
Nitroethane	16	100
Nitrogen, Liquified	23	
2-Nitrophenol	19	
4-Nitrophenol	19	
2-Nitroprenoi	16	
Nitrous Oxide	23	months and the same
Nonane	1	
Nonane		

^{*}See Table 2

Chemical Name	Chemical Class*	TLV (ppm)
Octane	1	500
Oil Edible: Coconut	22	
Oil Edible: Lard	22	
Oil Edible: Palm	22	
Oil Edible: Safflower	22	
Oil Edible: Tucum	22	
Oil Misc.: Croton	22	
Oil Misc.: Linseed	22	
Oil Misc.: Turbine	22	
Oxygen, Liquid	23	
Pentaborane	23	0.005
Paracetic Acid	7	
Perchloromethyl Mercaptan	2	0.1
Phosphorus Tribromide	23	
Piperazene	21	
Propiolactone, Beta	8	
Propionic Anhydride	7	
Propyleneimine, Inhibited	10	2
Propyl Mercaptan (n-)	12	
Silicon Tetrachloride	23	
Tetrachloroethane	2	5
Tetrafluoroethylene, Inhibited	2	
Thiophosgene	23	
Toluidene (o-)	14	5
Trichlorosilane	23	
Trifluorochloroethylene	2	
Triisobutylaluminum	23	
Trimethylchlorosilane	23	
Vanadium Oxytrichloride	23	
Vinyl Fluoride, Inhibited	2	
Vinyl Methyl Ether, Inhibited	3	
Vinyl Trichlorosilane	23	
Xyleno1	17	

^{*}See Table 2

Table C-3

PARTICULATES AND LOW VAPOR PRESSURE LIQUIDS FOR WHICH THE XM-41 FILTER IS ACCEPTABLE

Adiponitrile Alkylbenzenesulfonic Acids Aminoethanolamine (N-) Anisoyl Chloride Benzoic Acid Benzyl Alcohol Butylphenol (p-tert-) Caprolactam (Solution) Catechol Chloraniline (p-) 4-Chloro-o-Toluidine Copper Napthenate (IC) Creosote, Coal Tar Cyanoacetic Acid Decaborane Decahydronaphthalene Decyl Alcohol Decylbenzene (n-) Diethylene Glycol Monobutyl Ether Diethylene Glycol Monobutyl Ether Acetate Diphenyl Ether Dipropylene Glycol Ethylene Cyanohydrin Ethylene Glycol Monobutyl Ether Acetate Hexachlorocyclopentadiene Hexadecyl Sulfate, Sodium Salt Hexylene Glycol Hydroquinone Lactic Acid Lauroyl Peroxide Lauryl Mercaptan Linear Alcohols (12-15 Carbons) Maleic Hydrazine Methylcyclopentadier /lmonganese Tricarbony1 1-Napthylamine Nicotine Nonano1 Phenyldichloroarsine, Liq. Polychlorinated Biphenyls Quinoline Sulfuric Acid, Spent Toluene 2,4-Diisocyanate 1-Tridecene Triethanolamine

Table C-4

PARTICULATES FOR WHICH THE XM-41 FILTER IS ACCEPTABLE

Acridine
Acrylamide
Adipic Acid
Aldrin
Aluminum Chloride
Aluminum Fluoride
Aluminum Nitrate
Aluminum Sulfate
Ammonium Acetate
Ammonium Benzoate
Ammonium Bicarbonate
Ammonium Bifluoride
Ammonium Carbonate
Ammonium Chloride
Ammonium Citrate
Ammonium Dichromate
Ammonium Fluoride
Ammonium Formate
Ammonium Gluconate
Ammonium Hydroxide, 28% AQ
Ammonium Iodide
Ammonium Lactate
Ammonium Molybdate
Ammonium Nitrate
Ammonium Nitrate-Carbonate Mix
Ammonium Nitrate-Phosphate Mix
Ammonium Nitrate-Sulfate Mix
Ammonium Nitrate-Urea Solution
Ammonium Oleate
Ammonium Oxalate
Ammonium Pentaborate
Ammonium Perchlorate
Ammonium Persulfate
Ammonium Phosphate
Ammonium Silicofluoride
Ammonium Stearate
Ammonium Sulfamate
Ammonium Sulfate
Ammonium Sulfite
Ammonium Tartrate Ammonium Thiocyanate
Ammonium Thiosulfate
Amyltrichlorosilane (n-)
Anthracene
Antimony Potassium Tartrate
Antimony Trifluoride
Antimony Trioxide
Arsenic Acid
Arsenic Sulfide (DI)
Arsenic Trioxide
VIBERITE ILIUXIDE

Arsenic Trisulfide Asphalt Asphalt Blending Stocks:STR Atrazine Azinphosmethyl Barium Carbonate Barium Chlorate Barium Nitrate Barium Perchlorate Barium Permanganate Barium Peroxide Benzene Hexachloride Benzophenone Benzyl n-Butyl Phthalate Benzyl Chloroformate Benzyldimethyl-Octadecylammonium Chloride Benzyltrimethylammonium Chloride Beryllium, Metallic Beryllium Chloride Beryllium Fluoride Beryllium Nitrate Beryllium Oxide Beryllium Sulfate Bismuth Oxychloride Bisphenol A Bisphenol A Diglycidyl Ether Boiler Compound-Liquid Boric Acid Brucine 1,4-Butynediol Cacodylic Acid Cadmium Acetate Cadmium Bromide Cadmium Chloride Cadmium Fluoborate Cadmium Nitrate Cadmium Oxide Cadmium Sulfate Calcium Metallic Calcium Ar enate Calcium Carbide Calcium Chlorate Calcium Chloride Calcium Chromate Calcium Cyanide Calcium Fluoride Calcium Hydroxide Calcium Hypochlorite Calcium Nitrate

Calcium Oxide Calcium Peroxide Calcium Phosphate Calcium Phosphide Calcium Resinate Captan Carbarvl Caustic Potash Solution Caustic Soda Solution Chlordane Chloroacetophenone Chromic Anhydride Citric Acid Cobalt Acetate Cobalt Chloride Cobalt Nitrate Cobalt Sulfate Collodion Copper Acetate Copper Acetoarsenite Copper Arsenite Copper Bromide Copper Chloride Copper Cyanide Copper Fluoborate Copper Iodide Copper Nitrate Copper Oxylate Copper Sulfate Coumaphos Cupriethylenediamine Solution Cyclohexanyltrichlorosilane 2,4-D (Esters) DDD DDT Demeton Di-N-Amyl Phthalate Diazinon Dibenzoyl Peroxide Dibutylphenol Dibutyl Phthalate Di-(p-Chlorobenzoyl) Peroxide 2,4-Dichlorophenoxyacetic Acid 4,4-Dichloro-Alpha-Trichloromethyl-Benzhydrol 2,4-Dinitroaniline Dieldrin Diethanolamine Diethyl Phthalate

Diethylene Glycol

Di-(2-Ethylehexvl) Phosphoric Acid Diheptyl Phthalate Diisodecyl Phthalate Diisopropylbenzene Hydroperoxide Dimethylhexane Dihydroperoxide, Wet Dimethylpolysiloxane Dimethyl Terephthalate Dinitrobenzene (m-) Dinitrocresols 2,4-Dinitrophenol 2,4-Dinitrotoluene Dioctyl Adipate Dioctyl Phthalate Dioctyl Sodium Sulfosuccinate Diphenylamine Diphenyldichlorosilane Diphenylmethane Diisocyanate Dodecano1 Dodecy1benzene Dodecylbenzenesulfonic Acid, Calcium Salt Dodecylbenzenesulfonic Acid, Isopropylamine Salt Dodecylbenzenesulfonic Acid, Triethanolamine Salt Dodecyl Sulfate. Diethanolamine Salt Dodecyl Sulfate, Magnesium Salt Dodecyl Sulfate. Sodium Salt Dodecyl Sulfate, Triethanolamine Salt Dodecyltrichloroisilane Dowtherm Endrin Epoxidized Vegetable Oils Ethoxydihydropyran Ethoxylated Dodecanol Ethoxylated Nonylphenol Ethoxylated Pentadecanol Ethoxylated Pentadecanol Ethoxylated Tridecanol Ethoxy Triglycol Ethylenediamine Tetracetic Acid Ethylene Glycol Ethylhexyl Tallate Ferric Ammonium Citrate

Ferric Ammonium Oxalate

Ferric Chloride

Ferric Glycerophosphate

Ferric Nitrate Ferric Sulfate

Ferric Ammonium Sulfate

Ferrous Chloride
Ferrous Fluoborate
Ferrous Oxalate
Ferrous Sulfate
Fluosilicic Acid
Fluosulfonic Acid

Formic Acid Gallic Acid

Glycerine

Glycidyl Methacrylate

Formaldehyde Solution

Heptachlor

Hexadecyltrimethylammonium Chloride

Hexamethylenetetramine

Isodecyl Alcohol Isophthalic Acid

Isopropyl Percarbonate Latex, Liquid Synthetic

Lead Acetate
Lead Arsenate
Lead Fluoborate
Lead Fluoride
Lead Iodide
Lead Nitrate

Lead Tetraacetate Lead Thiocyanate

Litharge

Lithium Metal

Lithium Aluminum Hydride

Lithium Hydride

Magnesium

Magnesium Perchlorate

Malathion Maleic Acid Mercuric Acetate

Mercuric Acetate

Mercuric Ammonium Chloride

Mercuric Chloride Mercuric Cyanide Mercuric Iodide Mercuric Nitrate Mercuric Oxide Mercuric Sulfide

Mercurous Chloride Mercurous Nitrate Methanearsonic Acid, Sodium Salts

Methoxychlor Methyl Parathion

1-Methylpyrrolidone Molybdic Trioxide

Nabam

Nickel Acetate

Nickel Ammonium Sulfate

Nickel Bromide
Nickel Chloride
Nickel Cyanide
Nickel Fluoborate
Nickel Formate
Nickel Nitrate
Nickel Sulfate
Nicotine Sulfate

Nitraline

Nitrilotriacetic Acid & Salts

2-Nitroaniline 4-Nitroaniline Nonyl Phenol

Octyl Epoxy Tallate

Oleic Acid

Oleic Acid Potassium Salt Oleic Acid Sodium Salt

Oleum

Oxalic Acid Parathion

Pentachlorophenol
Pentadecanol
Pentaerythritol
Perchloric Acid
Petrolatum (Grease)

Phenylhydrazine Hydrochloride

Phosphoric Acid
Phosphorus, Red
Phsophorus, White
Phosphorus Oxychloride
Phosphorus Pentasulfide
Phthalic Anhydride

Polybutene .

Polyethylene Polyphenyl Isocyanate

Polyphosphoric Acid Polypropylene

Polypropylene Glycol

Polypropylene Glycol Methyl Ether

Potassium

Potassium Arsenate Potassium Binoxalate

Potassium Chlorate Potassium Chromate Potassium Cyanide Potassium Dichloro-S-Triazinetrione Potassium Dichromate Potassium Hydroxide Potassium Iodide Potassium Oxalate Potassium Permanganate Potassium Peroxide Propylene Butylene Polymer Pyrogallic Acid Resorcinol Salicylic Acid Selenium Dioxide Selenium Trioxide Silver Acetate Silver Carbonate Silver Fluoride Silver Iodate Silver Nitrate Silver Oxide Silver Sulfate Sodium Metallic Sodium Alkylbenzenesulfonates Sodium Alkyl Sulfates Sodium Amide Sodium Arsenate Sodium Azide Sodium Bisulfite Sodium Borate Sodium Borohydride Sodium Cacodylate Sodium Chlorate Sodium Chromate Sodium Cyanide Sodium Dichromate Sodium Dichloro-s-Triazinetrione Sodium Ferrocyanide Sodium Fluoride Sodium Hydride Sodium Hydrosulfide, Solution Sodium Hydroxide Sodium Hypochlorite Sodium Methylate Sodium Nitrite Sodium Oxalate Sodium Phosphate Sodium Silicate Sodium Silicofluoride

Sodium Sulfide

Sodium Sulfite Sodium Thiocyanate Sorbitol Stearic Acid Sulfolane Sulfur (Liquid) A 113° to 120°C Sulfuric Acid 2,4,5-T (Esters) Tallow Tallow Fatty Alcohol Tannic Acid Tetrabutyl Titanate Tetradecanol 1-Tetradecene Tetradecylbenzene Tetraethyl Dithiopyrophosphate Tetraethylene Glycol Tetraethylenepentamine Tetraethyl Pyrophosphate Thorium Nitrate Toluenesulfonic Acid (p-) Toxaphene Trichlorophenol 2.4.5-Trichlorophenoxyacetic Acid Trichloro-S-Triazinetrione Tricresyl Phosphate Tridecanol Triethylene Glycol Triethylenetetramine Triethylaluminum Trifluralin Tripropylene Glycol Tris (Aziridinyl) Phosphene Oxide Undecanol Undecylbenzene (n-) Uranyl Acetate Uranyl Nitrate Uranyl Sulfate Urea Urea Peroxide Vanadium Pentoxide Vanadyl Sulfate Wax: Carnauba Wax: Paraffin Zinc Acetate Zinc Ammonium Chloride Zinc Arsenate Zinc Borate Zinc Bromide

Zinc Chloride

Zinc Chromate

Zinc Dialkyldithiophosphate

Zinc Fluoborate

Zinc Nitrate

Zinc Phenolsulfonate

Zinc Phosphide

Zinc Silicofluoride

Zinc Sulfate

Zirconium Acetate

Zirconium Nitrate

Zirconium Oxychloride

Zirconium Sulfate

APPENDIX D FLAMMABLE VAPORS

The following substances are combustible in air, and have vapor pressures that approach or exceed 0.4% concentration in air at 38° C:

Acetaldehyde Acetic Acid Acetic Anhydride

Acetone Acetonitrile Acetylacetone Acetyl Bromide Acetyl Chloride Acetylene

Acetyl Peroxide Solution

Acrolein Acrylic Acid Acrylonitrile Allyl Alcohol Allyl Bromide Allyl Chloride Allylchloroformate Amyl Acetate (n-) Amyl Alcohol (n-)

Amyl Methyl Ketone (n-)

Benzaldehyde Benzene Benzonitrile Benzoyl Chloride Benzylamine Benzyl Bromide Benzyl Chloride Bromobenzene

Butadiene Inhibited

Butane

Butyl Acetate (n-) Butyl Acetate (sec-) Butyl Acrylate (iso-) Butyl Acrylate (n-) Butyl Alcohol (n-) Butyl Alcohol (sec-) Butyl Alcohol (tert-)

Butylamine (n-) Butylamine (sec-) Butylamine (tert-) Butylene Gas

1,2-Butylene Oxide

Butyl Hydroperoxide (tert-) Butyl Methacrylate (n-) Butyraldehyde (n-) Butvraldehyde (iso-) Butyric Acid (n-)

Camphene

Carbon Disulfide Carbon Monoxide

Carene

Chlorobenzene Chloroform

Chlorohydrin (Crude) Chloromethyl Methyl Ether

Crotonaldehyde

Cumene Cyanogen Cyclohexane Cyclohexanol Cyclohexanone

Cyclohexanone Peroxide

Cyclohexylamine Cyclopentane Cyclopropane Cymene (P-) 1-Decene

Diacetone Alcohol Di-N-Butylamine Di-N-Butyl Ether Di-N-Butyl Ketone Dichlorobenzene (0-) Dichlorobenzene (P-)

Dichlorobutene

1,2-Dichloroethylene Dichloropropane (1,2-)

Dichloropropene 1,1-Difluoroethane 1,1-Dimethylhydrazine Dicyclopentadiene Diethylamine Diethylbenzene

Diethyl Carbonate

Diethylene Glycol Dymethyl Ether

Diisobutylcarbinol Diisobutylene Diisobutyl Ketone Diisopropanolamine Diisopropylamine Dimethylacetamide Dimethylamine Dimethyl Ether Dimethyl Sulfide

Dioxane (1,4-) Dipentene

Distillates: Flashed Feed Stocks

Epichlorohydrin

Ethane

Ethyl Acetate Ethyl Acetoacetate Ethyl Acrylate Ethyl Alcohol

Ethylamine
Ethylbenzene
Ethyl Butanol
Ethyl Butyrate
Ethyl Chloride
Ethyl Chloroacetate
Ethyl Chloroformate
Ethylene

Ethylenediamine Ethylene Dibromide Ethylene Dichloride

Ethylene Glycol Diethyl Ether Ethylene Glycol Dimethyl Ether Ethylene Glycol Monoethyl Ether Ethylene Glycol Monoethyl Either

Acetate

Ethylene Glycol Monomethyl Either

Ethyleneimine
Ethylene Oxide
Ethyl Ether
Ethyl Formate
Ethylhexaldehyde
Ethylidenenorbornene

Ethyl Lactate Ethyl Mercaptan Ethyl Nitrite

2-Ethyl-3-Propylacrolein Formaldehyde Solution

Formic Acid Furfural

Gas Oil: Cracked
Gasoline: Automotive
(4.23G PB/Gal)
Gasoline: Aviation

Gasoline: Aviatio (4.86G PB/Gal)

Gasoline: Casinghead Gasoline: Polymer Gasoline: Straight Run Gasoline Blending Stocks:

Alkylates

Gasoline Blending Stocks:

Reformates Heptane Heptanol 1-Heptene

Hexaldehyde (n-1)

Hexane Hexanol 1-Hexene Hydrazine

Hydrogen, Liquified Hydrogen Sulfide Hydroxypropyl Acrylate

Isoamyl Alcohol

Isobutane

Isobutyl Acetate
Isobutyl Alcohol
Isobutylamine
Isobutylene
Isobutyric Acid
Isobutyronitrile

Isohexane Isopentane Isoprene

Isopropyl Acetate
Isopropyl Alcohol
Isopropylamine
Isopropyl Ether
Isopropyl Mercaptan
Isovaleraldehyde

Jet Fuel: JP-1 (Kerosene)

Jet Fuel: JP-3 Jet Fuel: JP-4

Kerosene

Liquified Natural Gas Liquified Petroleum Gas

Mesityl Oxide Methallyl Chloride

Methane Methyl Acetate Methylacrylate Methyl Alcohol Methylamine

Methyl Amyl Alcohol Methyl-n-Butyl Ketone

Methyl Chloride
Methyl Chloroformate
Methylcyclopentane
Methyl Ethyl Ketone
Methylethylpyridine

Methyl Formal Methyl Formate Methyl Hydrazine

Methyl Isobutyl Carbinol Methyl Isobutyl Ketone Methyl Isopropenyl Ketone,

Inhibited

Oil Misc: Motor Methyl Mercaptan Methyl Methacrylate Oil Misc: Neatsfoot Oil Misc: Penetrating Methylstyrene, Alpha Oil Misc: Range Methyl Vinyl Ketone Oll Misc: Resin Mineral Spriits Oil Misc: Road Morpholine Oil Misc: Rosin Naphtha: Coal Tar Naphtha: Solvent Oil Misc: Sperm Oil Misc: Spindle Naphtha: Stoddard Solvent Oil Misc: Spray Naphtha: VM + P (75 Naphtha) Oil Misc: Tall Neohexane Nickel Carbonyl Oil Misc: Tanner's Oil Misc: Transformer Nitroethane Oil Misc: Turbine Nitromethane Paraformaldehyde 2-Nitropropane Nonane Pentane Nonene 1-Pentene Petroleum Naphtha 1-Nonene Pheno1 Octane Propane 1-Octene Oil: Clarified Propionaldehyde Propyl Acetate (n-) Oil: Crude Propyl Alcohol (n-) Oil: Diesel Oil Edible: Castor Propylene Propylene Glycol Methyl Ether Oil Edible: Coconut Propyleneimine, Inhibited Oil Edible: Cottonseed Propylene Oxide Oil Edible: Fish Oil Edible: Lard Propylene Tetramer Propyl Mercaptan (n-) Oil Edible: Olive Pyridine Oil Edible: Palm Styrene Oil Edible: Peanut Oil Edible: Safflower Tetraethyl Lead Tetrahydrofuran Oil Edible: Soya Bean Tetramethyl Lead Oil Edible: Tucum Toluene Oil Edible: Vegetable Oil Fuel: No. 1 (Kerosene) Toluidene (o-) Triethylamine Oil Fuel: No. 1-D Trimethylamine Oil Fuel: No. 2 Oil Fuel: No. 2-D Turpentine Valeraldehyde Oil Fuel: No. 4 Oil Fuel: No. 5 Vinyl Acetate Oil Fuel: No. 6 Vinyl Chloride Oil Misc: Absorption Vinyl Fluoride, Inhibited Oil Misc: Coal Tar Vinylidenechloride, Inhibited Oil Misc: Croton Vinyl Methyl Ether, Inhibited 011 Misc: Linseed Vinyltoluene Oil Misc: Lubricating Xylene (m-) Oil Misc: Mineral Xylene (o-) Oil Misc: Mineral Seal Xylene (p-)